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PYRITE STABILITY RELATIONS IN THE Fe–S SYSTEM

G. KULLERUD AND H. S. YODER

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ABSTRACT

The reaction pyrite $\rightleftharpoons$ pyrrhotite + liquid (or gas) was investigated up to 5,000 bars [1] by means of a new technique. The univariant equilibrium curve for the reaction originates at an invariant point 743° C and about 10 bars and passes through the points 748° C, 335 bars; 755°, 1,000 bars; 770°, 2,000 bars; and 810°, 5,000 bars.

The relations of pyrite in the Fe-S system are deduced from thermodynamic principles and available data. The limitations of the various experimental techniques for sulfide systems are analyzed in the light of the pressure-temperature diagram for the Fe-S system. The apparently large effect of iron in the vapor or gas of the system is described.

The occurrence of primary pyrite in some gabbros, amphibolites, and granites and not in basalts and rhyolites is accounted for by comparing the upper stability curves of pyrite at various partial pressures of sulfur with the beginning of melting curves of rocks of basaltic and granitic compositions under hydrous conditions. When the partial pressure of sulfur is less than about 10 bars small changes in its value have a great effect on the stability of pyrite. The relations of pyrite in the Fe-S system indicate that massive pyrite bodies could not have crystallized directly from a liquid of pyrite composition.

INTRODUCTION

PYRITE is the most abundant of the sulfides and occurs under a wide range of geological conditions. It is known to form in many sediments, in all grades of metamorphic rocks, in most intrusive igneous rocks, and rarely in

[1] One bar = 0.987 atm. = 14.504 psi = 1.0197 kg/cm^2 = 750.06 mm Hg.

extrusive igneous rocks. Although pyrite is the principal constituent of many ore bodies, its absence in some deposits believed to have formed at high temperatures from liquids or gases of the requisite composition suggests that the mineral is restricted in occurrence under some conditions. The purpose of this investigation was to determine experimentally the maximum stability limits for pyrite and to correlate its occurrence with these limits.

NATURAL FeS_2

Natural material of the composition FeS_2 or close to FeS_2 is reported to occur in two crystalline modifications, pyrite and marcasite. Pyrite has a cubic structure, $T_h^6 = Pa3$ according to Bragg (14), and is commonly found as cubes, often as pyritohedra, and more rarely as octahedra (88, 95, 83). Marcasite has an orthorhombic structure, $V_h^{12} = Pnnm$ according to Buerger (15), and is commonly tabular, often pyramidal, and less commonly prismatic in habit (62, 30). Pyrite and marcasite commonly occur together (41) either intergrown or in alternating concentric layers (85). They have been considered as polymorphs, that is, materials of exactly the same composition possessing different crystal structures. Some recent studies by Buerger (16), and Smith (81) have cast doubt on the contention that pyrite and marcasite have the same composition. It is relevant to the following arguments to evaluate these doubts.

Pyrite

Chemical Analyses.—A compilation by Doelter and Leitmeier (20, p. 529) of chemical analyses of pyrite made in the period 1849–1920 indicated that the iron-to-sulfur ratio is 1 : 2. The small deviations from this ratio were attributed by them to analytical errors. Buerger (16) critically reviewed the analyses of pyrite up to the year 1932 and concluded "that pyrite corresponds very closely to ideal FeS_2. . . ." Smith (81), apparently unaware of Buerger's study, considered the deviations in these analyses as well as those in ten new analyses as real and stated that the ratio of iron to sulfur in pyrite varies from 1 : 2.01 to 1 : 1.94. On the basis of density and cell volume measurements iron was thought by Peacock and Smith (65) to replace some sulfur in the ideal structure. Because of this difference of opinion, the preparation of some of the samples and analytical procedures of these authors are again reviewed.

Of the eight previously published analyses listed by Smith (81, p. 8, Table I), three are on specimens from Elba, presumably from the famous locality Rio Marina. As Allen, Crenshaw, and Merwin (3) clearly noted, and Buerger (16, p. 48) reemphasized, the pyrite from this locality contains inclusions of hematite. Chemical analysis of the residue after removal of this hematite yields $FeS_{2.00}$ (4). Smith (65) analyzed the Elba material without stating whether or not hematite was present and obtained $FeS_{1.98\pm0.01}$. On another occasion Smith (82, p. 520) mentioned the occurrence of hematite with the Elba pyrite. For this reason the work of Allen, Crenshaw, Johnston, and Larsen (2) still stands as the only unquestionable analysis of the Elba pyrite, which is $FeS_{2.00}$. Only one (Miniera di Casall, Prov. Grosseto) of

the remaining published analyses given by Doelter and Leitmeier (20) and listed by Smith (81, Table I, no. 1) survived Buerger's critical review, and this analysis was made prior to the publication of the refinements of sulfur analysis established by Allen and Johnston (4). According to Dr. E. G. Zies (personal communication, 1957), who worked with Allen and Johnston, the analysis of sulfur is precise only to ± 0.2 weight percent after all corrections are made. The difference in sulfur content of $FeS_{2.00}$ and $FeS_{1.98}$, for example, is 0.25 weight percent. In the six new analyses made for Smith (81, p. 9) by L. J. Rogers the totals were low (96.5–99.0) since only Fe and S were determined, and with one exception the alleged sulfur deficiency is greater the lower the total, a strong indication of contamination. The iron-to-sulfur ratios of four additional new analyses, also incomplete, made by Smith himself, were tabulated. No data on the source and purity of the specimens or the details of the analyses were given.

TABLE 1

CELL DIMENSIONS OF NATURAL PYRITE

	a_0 in Å*	
	Leadville, Colo.	Rio Marina, Elba
Peacock and Smith (65)	5.4176 ± 0.0003†	5.4160 ± 0.0003†
Kerr, Holmes, and Knox (48)	5.4177 ± 0.0001†	—
Gordon (31)	5.4179 ± 0.0003	—

* Conversion factor 1 Å = 1.002034 kX.
† Corrected by Wasserstein (97).

This review of the evidence strongly suggests that variations in the metal-to-sulfur ratio of pyrite are occasioned by inadequate analytical techniques, impure samples, or both.[2]

Cell Dimensions.—The unit cell dimensions have also been taken as a measure of the composition. Peacock and Smith (65) found a difference in the unit cell dimensions of pyrite from Leadville, Colorado, and from Rio Marina, Elba, by X-ray powder diffraction studies (Table 1). Measurements by Kerr, Holmes, and Knox (49) and Gordon (31) confirm the value of a_0 for the Leadville material. Allen, Crenshaw, Johnston, and Larsen (2) note that a Leadville sample analyzed by them contains 0.1 percent Cu. In addition Lepp (53) reports that the unit cell dimension of synthetic pyrite is 5.4176 ± 0.0003 Å, and in two experiments synthetic pyrite formed in equilibrium with pyrrhotite gave 5.4165 and 5.4163 ± 0.0007 Å.[3] In view

[2] It is to be noted as a consequence of this conclusion that the variation in electrical resistance attributed by Smith (81) to sulfur deficiency must be considered invalid. Its use as a measure of the temperature of formation of pyrite (80, 82) has already been shown to be without foundation by Sasaki (77), Fischer and Hiller (24), and others.

[3] It should be noted that the pyrite believed by Lepp to have formed in the absence of pyrrhotite was made in a sealed tube from *stoichiometric* quantities of iron and sulfur (Exp. No. L-55). The pyrite formed under these conditions cannot be the only phase present because the free space in the tube contains a sulfur-rich vapor that results from the breakdown of a small amount of pyrite to $Fe_{1-x}S + V$. If the volume of free space, not indicated by Lepp, is small it may be difficult to observe the pyrrhotite.

of the character of X-ray diffraction patterns of synthetic materials, the assigned errors of measurement, and influence of temperature on cell dimensions, the present writers do not believe that the data obtained by Lepp are significantly different. The differences in cell dimensions of natural pyrites, if real, are more likely due to the presence of other atoms (e.g., Ni, Co, Cu, As, Se) rather than variations in the iron-to-sulfur ratio.

On the basis of present chemical analyses and cell measurements, it is believed that within the error of detection pyrite has a metal-to-sulfur ratio of 1 : 2.00.

Marcasite

Chemical Analyses.—Doelter and Leitmeier (20, p. 566–567) concluded from their compilation up to 1924 of analyses of marcasite that the mineral has the composition FeS_2. A more recent analysis given by Carmichael (18) supported this view. Buerger (16) critically reviewed eight published analyses, discarded six of them, and obtained an average iron-to-sulfur ratio of 1 : 1.990 from the remaining two analyses. In 1939 Berman (64, p. 315) commented as follows on Buerger's conclusion with regard to the composition of marcasite: "The deviation from the theoretical composition FeS_2 is probably within the limits of analytical errors." The present writers are in accord with Berman's statement.

TABLE 2

CELL DIMENSIONS OF MARCASITE IN Å* (DONNAY AND NOWACKI, 21)

	Frielinghaus (28)	de Jong (45)	Buerger (15)	Bannister (11)	Buerger (17)
a	4.41	4.46	4.45	4.45	4.445
b	5.36	5.43	5.40	5.40	5.425
c	3.36	2 × 3.402	3.38	3.39	3.388

* Conversion factor 1 Å = 1.002034 kX.

Cell Dimensions.—If the composition of marcasite does indeed vary, then the cell dimensions may also vary. The published cell dimensions of marcasite are listed in Table 2. The parameters of Buerger (17) in 1937 were obtained on the same material studied by him in 1931. In his 1934 report (16) he believed the *c* dimension (*a* of Buerger) was significantly different from that of a crystal studied by Bannister in 1932 (11) and suggested that the *c* dimension "shrinks with increasing iron content, without great effect on the other axes. . . ." In view of his more precise study of 1937 this conclusion is no longer valid. On the basis of the data in Table 2, taking into account the precision of the methods of measurement used, the various specimens are believed to have the same cell dimensions.

The chemical analyses and cell dimensions indicate, therefore, that the composition of marcasite does not deviate in the iron-to-sulfur ratio from 1 : 2.00 within the errors of measurement.

On the basis of the above review and analysis, it is concluded that both

pyrite and marcasite have the composition $FeS_{2.00}$, and that they are polymorphs.

PREVIOUS EXPERIMENTAL STUDIES

Previous attempts to outline experimentally the stability limits of pyrite have centered about three different approaches: solid state or wet chemical synthesis, thermal decomposition, and inversion of marcasite.

Synthesis.—The synthesis of pyrite was reported by Proust as early as 1803 (67), when iron and sulfur or FeS and sulfur were heated together at temperatures "below red heat." Pyrite has also been reported often in solid state experiments as one of the phases to form in multicomponent systems (see for example Merwin and Lombard, 56). The formation of marcasite in similar experiments has not been reported.

Preparation by means of various wet chemical methods has been described principally by Allen, Crenshaw, Johnston, and Larsen (2), and Allen, Crenshaw, and Merwin (3). According to these workers the action of H_2S on ferric sulfate or chloride, for example, in weakly acid, neutral, or alkaline solutions yields mostly pyrite; while solutions of high acidity at low temperatures precipitate mainly marcasite. With the exception of one experiment (3, p. 397, Table I, no. 3) at 25° C in which only marcasite was believed to be precipitated, both pyrite and marcasite were obtained as products. The products were identified by the Stokes (85) oxidation method. In similar experiments at 20° C, Rosenthal (74) identified his products by X-ray powder diffraction patterns and obtained only marcasite in acid solutions and only pyrite in basic solutions.

Decomposition.—Cusack (19) in 1898 observed that pyrite "suddenly decomposed at 642°; whether it is fused at that temperature or not it is impossible to say. . . ." Later it was found that pyrite on heating decomposes into pyrrhotite and vapor. This dissociation was reported by Kothny (50) in 1911 to begin at about 200° C in an inert gas stream; a vapor pressure of 1 atm. was reached at about 700° C. Barth (12) in 1912 found that dissociation begins at about 350° C in a closed tube and that 1 atm. vapor pressure obtains at 600° C. In the same year Hempel and Schubert (39) found dissociation to be measurable in closed tubes at 480° C, but they did not specify the temperature at which the dissociation pressure reached 1 atm. Allen and Lombard (5) in 1917 obtained the dissociation temperatures of natural pyrite in the presence of sulfur vapor at pressures up to 680 mm Hg. Later Raeder (68) in 1929, D'Or (22) in 1931, Juza and Biltz (46) in 1932, and Rudder (75) in 1936 redetermined the dissociation pressures of natural pyrite by essentially the same methods. Jensen (43) in 1942 believed that pyrite "is able to crystallize out first from an iron-sulfur melt. . . ." He was of the opinion that pyrite and pyrrhotite formed a eutectic at about 1000° C. In 1954 Rosenqvist (73), although presenting a phase diagram in which pyrite and pyrrhotite form a eutectic, came to the conclusion on the basis of an extrapolation of his data on the Fe-S system that at about 800° C "pyrite would undergo a peritectic decomposition to give pyrrhotite and

liquid sulfur." These experiments and opinions will be reviewed below in the light of the new data to be presented.

Inversion.—Marcasite and pyrite are commonly found together in nature, sometimes intergrown in concentric layers. Mixtures of pyrite and marcasite were obtained in experiments at temperatures as high as 300° C (2). However, because of the long period of time required to attain the temperature in the thick-walled pressure vessels, marcasite may have grown at lower temperatures and persisted metastably at the run temperature. It cannot be said with certainty, therefore, that marcasite is stable up to 300° C (3, p. 408–410). On the other hand, when marcasite is heated at 450° C in an evacuated glass tube, it changes very slowly to pyrite. According to Allen (1) no change could be detected at 400° C in a period of 4 hours. Anderson and Chesley (7) heated synthetic marcasite in glass tubes for 5 hours and found no change at 405° C, about 50 percent pyrite at 415° C, and complete inversion to pyrite at 425° C. They were also able to convert marcasite into pyrite by grinding at room temperature. Kullerud (unpublished data, 1956) found that in 2 weeks' time at 400° C marcasite inverted to pyrite. He observed no change in marcasite at 350° C held for six months. It was not possible to invert pyrite to marcasite at any temperature. It may be concluded tentatively, therefore, that the field of stability of pyrite extends to temperatures at least as low as 400° C and presumably lower. Because of the sluggish nature of the inversion, it is not possible from these data to delineate the field of stability of marcasite.

METHODS OF INVESTIGATION

The stability of pyrite was investigated by holding synthetic mixtures (on and close to the requisite composition), natural pyrite, and natural marcasite at fixed temperatures and pressures for various periods of time. Two techniques were employed; one involves the use of rigid silica tubes, and the other, collapsible metal tubes. The products were quenched and identified at room temperature by magnetic, optical, and X-ray determinative methods.

Starting Materials

Mixtures of iron and sulfur of high purity were used in the synthesis of pyrite. No catalytic agents or additional components were employed. Experiments using these materials were carried out first using iron and sulfur in the ratio of 1 : 2 with a very slight excess of sulfur. The reaction of these yielded grains of pyrrhotite which reacted with some of the remaining sulfur to form pyrite. The grains of pyrrhotite were thereby covered with a shell of pyrite, retarding further reaction. For this reason iron and sulfur were first mixed in 5-gram batches in the ratio of exactly 1 : 1 and held at 550–600° C in closed silica tubes for 1 week to form troilite. Since the vapor pressure of troilite at this temperature is exceptionally low, the loss of sulfur and iron to the vapor was negligible for the volume of free space allowed. Sulfur was then mixed with troilite, finely ground under acetone, so that the iron-to-

sulfur ratio was 1:2 with a slight excess (<0.15 percent by weight) of sulfur to compensate for the very small loss of sulfur to the vapor. In this way the rate of formation of pyrite was increased in the regions where it is stable.

Iron.—The iron was obtained from the National Bureau of Standards, Standard Sample 55d, open-hearth iron. The analysis of this material shows it to consist of 99.84 percent Fe. The principal contaminants are:

Cu	0.056	As	0.009	N	0.004
Mn	0.030	Co	0.007	Al	0.002
S	0.014	Cr	0.005	Mo	0.001
C	0.010	P	0.005	Si	<0.001
Ni	0.010	Sn	0.005	V	<0.001

in weight percent. The grain size of the material as received was about 1 to 2 mm. Reaction rates were high, so no further reduction in size was necessary.

Sulfur.—The sulfur was obtained from Dr. W. N. Tuller, Superintendent of Laboratory, Freeport Sulphur Co., Port Sulphur, Louisiana, and has only 0.007 percent impurities, all of which is carbonaceous material.

Pyrite.—The same natural pyrite from Leadville, Colorado, studied by Allen, Crenshaw, Johnston, and Larsen (2, p. 177) was used in some of the present experiments. They indicated the pyrite contained 0.1 percent Cu. Independent partial analyses of samples from the same locality by Smith and by Rogers (81, p. 9, no. 26) gave $FeS_{2.00}$ and $FeS_{2.01}$, respectively. In other experiments an analyzed pyrite from Nordsynken Mine, Sulitjelma, Norway, was used. The analysis by H. B. Wiik on this material shows that it has a composition which, when maximum possible analytical errors are considered, lies within the limits of $FeS_{2.00\pm0.01}$. The powder X-ray diffraction patterns of these samples agree with the published pattern cited below. A study of polished sections of the powdered natural materials indicated no other phases were present.

Marcasite.—The marcasite used in the inversion studies was an unanalyzed sample from Joplin, Missouri. An analysis of similar material from the same locality gave $FeS_{2.00}$ (4). The crystals exhibited the characteristic cockscomb habit that results from repeated twinning on {101}. The X-ray powder diffraction spacings were in accord with the composite data compiled in the American Society for Testing Materials X-ray Diffraction Data in 1955 (6).

Equipment

Rigid Tube.—All experiments at pressures below approximately 100 bars were carried out in evacuated silica glass tubes in the manner described by Kullerud (52, p. 72–73). The glass tubes are rigid and essentially of fixed volume. The free space within the tube, usually half filled with the starting materials, was reduced by placing closely fitting short silica-glass rods over the charge. The tubes are held in regulated furnaces at temperatures believed to be accurate to $\pm 2°$ C. The outside wall of the tube was at 1 atm.;

no external supporting pressure medium was employed. The vapor pressure inside the tube is not known; however, it is known to be less than that of pure sulfur at the same temperature (see, for example, Allen and Lombard, 5). In those runs where both liquid and vapor are present the maximum pressure can be estimated from the pure sulfur vapor pressure curve. Unfortunately, even the vapor pressure curve for pure sulfur is at best an approximation in the temperature range of interest. The pure sulfur vapor pressure curve given in Figure 1 was constructed from the measured sulfur vapor pressures

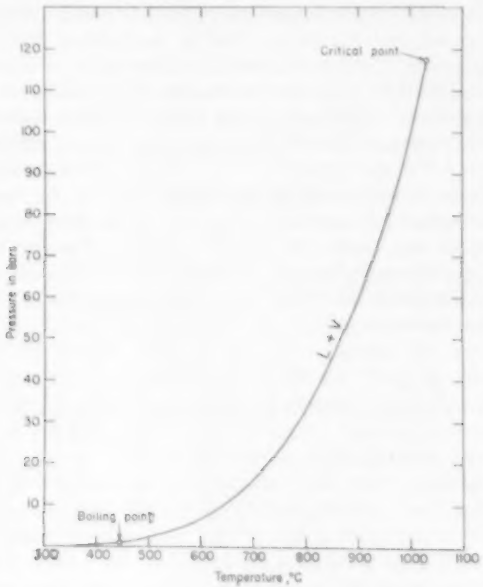

FIG. 1. Liquid ⇌ vapor curve for pure sulfur based on the measured sulfur vapor pressures in the range 100°–550° C (99) and the extrapolation of J. R. West (100) to the observed critical temperature of 1,040° ± 5° C (70) and an averaged critical pressure of 118 ± 31 bars.

in the range 100–550° C (99) and the extrapolation of J. R. West (100) to the observed critical temperature of 1,040° ± 5° C (70, p. 147) and an averaged critical pressure of 118 ± 31 bars based on various approximation methods.

Collapsible Tube.—A different technique was employed to investigate a greater range of pressures than that which could be estimated from the pure sulfur vapor pressure curve. Considerable success has been attained in the synthesis of hydrous minerals at high water pressures using sealed collapsible metal tubes. In these syntheses the pressure on the sample is fixed by applying a known pressure on the tube wall by means of a gas or liquid such as

H_2O, A, or CO_2. In this way the pressure on the sample is made essentially equal to the applied pressure through the malleable metal wall. The metals commonly used in hydrothermal synthesis are Pt, Au, and Ag. It was necessary to find a suitable malleable metal easy to weld which did not react with sulfur to adapt the technique to the investigation of sulfide systems. The sulfides of Pt and Ag were found to be stable at least as high as 800° C, and therefore these metals were not satisfactory containers. The sulfides of gold, on the other hand, were not stable above 240° C according to *Gmelin's Handbuch der anorganischen Chemie* (29). The sulfides of gold, Au_2S, AuS, and Au_2S_3, were reported to decompose at 240°, 140°, and 197–200° C, respectively. It appeared that Au tubes could be used above 240° C without loss of sulfur from the sample or destruction of the tube as a container. Subsequent runs at 300–900° C showed that no gold sulfides were formed during the run or the quench. The use of gold tubes, therefore, permits the investigation of sulfide systems over a wide range of pressures and temperatures.

Runs at 335, 1,000, and 2,000 bars were carried out in "cold-seal" pressure vessels, similar to those described by Tuttle (90). The temperatures and pressures were controlled within ± 5° C and ± 30 bars, respectively. The confining pressure was applied by means of H_2O. Runs at 5,000 bars were carried out in an internally heated pressure vessel (101) wherein argon gas is the pressure medium. In these runs the temperature was controlled to ± 5° C and the pressure varied ± 20 bars.

Quench Procedure

The phases formed at elevated pressures and temperatures were quenched by dropping the temperature to that of the room as quickly as possible. The rigid tubes were withdrawn from the furnace with tongs and plunged into water. It is believed that room temperature is reached in a few seconds. The pressure falls at a rate dependent on the temperature and free space in the tube. The collapsible tubes in the cold-seal pressure vessels were quenched in about 2 to 3 minutes by spraying the vessels with compressed air until the temperature fell below about 400° C and then with water until cold. The collapsible tubes in the internally heated pressure vessel were quenched by turning off the power to the furnace. The pressure vessel is continuously cooled by water, so room temperature is reached in about half a minute. The pressure in the cold-seal and internally heated pressure vessels was maintained constant during the quench.

The rate of quenching influences the nature of the products. The observed effects are given under Description of Phases.

Identification of Phases

The products obtained were identified at room temperature by their macroscopic physical properties, optical properties in reflected light, and X-ray powder diffraction patterns.

Physical Properties.—Pyrite is usually recognized by its brass-yellow color. However, when very fine grained it appears dark gray and is difficult

to distinguish from pyrrhotite. Pyrrhotite is commonly dark gray in color and often forms prismatic crystals. Sulfur is easily recognized by its cream white, yellow, or green color. Single crystals are occasionally formed.

The magnetic behavior of some of the phases is often a useful means of identification. Juza and Biltz (46) studied the variation of magnetic properties of pyrrhotite as a function of composition. Troilite (FeS) showed no attraction to the magnet, whereas pyrrhotites ($Fe_{1-x}S$) showed a maximum of magnetic susceptibility at $Fe_{0.89}S$. The pyrrhotites formed in equilibrium with or by decomposition of pyrite were magnetic. Thus a small hand magnet served as a useful tool in distinguishing pyrrhotite from essentially nonmagnetic pyrite.

Optical Properties.—In reflected light pyrite has a yellowish-white color. It is isotropic, but some show definite anisotropism, which is believed to be due to deformation resulting from polishing (84). Pyrrhotite in polished sections has a cream color with a tint of pinkish brown, and it is strongly anisotropic and weakly pleochroic.

X-ray Pattern.—The products obtained were also readily identified by their X-ray powder diffraction patterns. The pattern for natural pyrite was given by Anderson and Chesley (7) in 1933, Harcourt (36) in 1942, and Kerr (48) in 1945. Swanson, Gilfrich, and Ugrinic (86, p. 30) in 1955 gave a pattern for synthetic pyrite. A few additional spacings, presumably due to impurities, appear in some patterns for natural pyrite which do not appear in synthetic pyrite. The pattern for synthetic hexagonal pyrrhotite was given by Haraldsen (35, p. 173) in 1941, and it agrees well with that of a natural hexagonal pyrrhotite given by Harcourt (36, p. 94) in 1942. The composition of pyrrhotite may be estimated by the d_{102} determinative curve of Arnold (8, p. 177). The pattern of the orthorhombic form of sulfur is given by the National Bureau of Standards (personal communication from M. I. Cook, 1957). There were no additional spacings such as those indicated by Pinkus, Kim, McAtee, and Concilio (66) for "insoluble" sulfur ($= \mu$ sulfur).

EXPERIMENTAL RESULTS

The results of most of the experiments designed to fix the upper stability limit of pyrite are compiled in Tables 3–7. Because the interpretation of the results is dependent on the nature of the experiment and the attainment of equilibrium, a few comments on some of the runs are required.

Silica Tube Runs.—In Table 3a it is seen that the rate of reaction of iron and sulfur to form pyrite is very slow. It was on the basis of these experiments that synthetic troilite and sulfur were used as starting materials in subsequent experiments.

The experiments in Table 3b indicate that pyrite melts incongruently to pyrrhotite, liquid, and vapor at $743° \pm 2°$ C at the vapor pressure of the system. Only the solid products obtained after quenching are recorded. No distinction could be made between sulfur resulting from the crystallization of the liquid and that from the vapor phase. The vapor phase is negligible

TABLE 3

RESULTS OF RUNS IN SILICA GLASS TUBES USING VARIOUS STARTING MATERIALS. PRESSURE, NOT MEASURED, IS THAT OF THE SYSTEM.

T, °C	Time, hrs.	Products*	*T*, °C	Time, hrs.	Products*
		(a) Iron + 2 sulfur			
500	2,400	Po + S + Py (<10%)	400	1,536	Po + S + Py (<5%)
500	1,200	Po + S + Py (< 5%)			
		(b) Synthetic troilite + sulfur			
750	1	Po + S	600	1,200	Py
745	1¼	Po + S	600	1,200	Py
740	1	Po + Py + S	500	168	Py
730	404	Py + Po + S	400	2,400	Py
700	720	Py + Po + S	300	2,880	Py
680	2 min.	Py + trace Po	200	4,000	Py
650	950	Py + trace Po			
		(c) Synthetic troilite + sulfur in excess			
760	235	Po + S	725	1 min.	Py + S
750	23½	Po (lamellae) + S	725	168	Py + S
750	166	Po + S	725	720	Py + S
742	312	Py + S			
		(d) Synthetic pyrite + sulfur in excess			
760	235	Po + S	745	23½	Po + S
750	166	Po + S	742	312	Py + S
		(e) Natural pyrite + sulfur in excess			
760 C†	235	Po + S	745 C	23½	Po + S
760 N	235	Po + S	745 N	23½	Po + S
750 C	166	Po + S	742 C	312	Py + S
750 N	166	Po + S	742 N	312	Py + S
		(f) Natural marcasite			
400	2,600	Py	350	336	M
400	772	Py + M	205	387	M
400	336	M + Py	150	504	M
400	168	M			
		(g) Natural marcasite + sulfur in excess			
400	336	Py + S	350	672	M + S

* Py = pyrite, Po = pyrrhotite, S = sulfur, M = marcasite.
† C = Leadville, Colorado; N = Sulitjelma, Norway.

in amount (43, p. 698) and may not be perceptible. Attention is directed to the 2-minute run at 680° C. The silica tube was placed in a furnace at 680° C, the sample reaching temperature within seconds, held for 2 minutes, and quenched in a water bath. In this short period of time there was almost complete reaction to pyrite. In the runs at 680° C and below no sulfur was observed among the quench products. Below 600° C no pyrrhotite was observed. As will be seen later equilibrium requires three phases, pyrite + pyrrhotite + vapor, for this bulk composition at these temperatures and pressures. Failure to observe all of the required phases is attributed to their minute quantity rather than their absence due to lack of equilibrium.

TABLE 4

RESULTS OF RUNS IN GOLD TUBES USING VARIOUS STARTING MATERIALS AT A PRESSURE OF 335 BARS

T, °C	Time, hrs.	Products	T, °C	Time, hrs.	Products
(a) Synthetic troilite + S					
750	356	Po + S + (Py)	725	336	Py
(b) Synthetic troilite + S in excess					
800	480*	Po (n.l.) + S + (Py)	750	784	Po + S + (Py)
750	356	Po + S + (Py)	725	336	Py + S
750	360	Po + S			
(c) Synthetic pyrite					
800	480*	Po (n.l.) + S + (Py)	750	784	Po + S
750	360	Po + S	750	784	Po + S
750	360	Po + S	725	336	Py

* Cooled slowly; not quenched; (n.l.) = no lamellae; (Py) = pyrite rims and blebs.

The results of Tables 3c, 3d, and 3e confirm the incongruent melting of pyrite to pyrrhotite + liquid + vapor, and the best value is taken to be 743° ± 2° C.

The data in Tables 3f and 3g suggest that pyrite is the stable form of FeS_2 to temperatures at least as low as 400° C. In view of the slow rate of transition at 400° C, it is likely that the rate is negligible below 400° C. It is not known whether or not marcasite has a field of stability at some temperature less than 400° C under the conditions of the experiment.

Runs at 335 Bars.—In Tables 4a, 4b, and 4c it is seen that pyrite breaks down between 725° and 750° C. The pyrite in some of the runs at 750° and 800° C, enclosed in parentheses, occurred as blebs in, or rims around, pyrrhotite, and is considered a quench product. The textural relations are shown in Figure 2. In order to test this interpretation, a run was made at 800° C and the pressure vessel was allowed to cool in air without applying

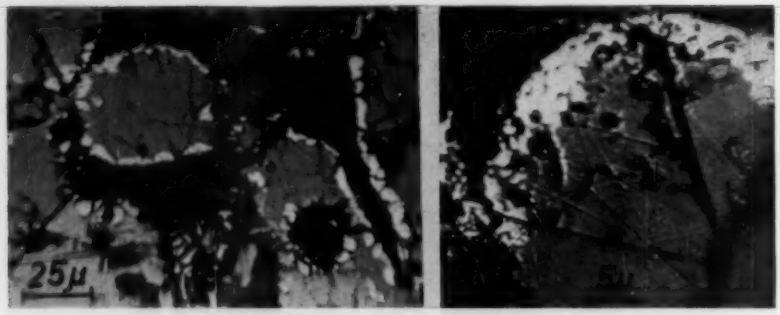

FIG. 2. (Left) Pyrite rims and blebs (white) around and in pyrrhotite grains (gray) formed during the quenching period of steel pressure vessel. The run was made at 850° C, 1,000 bars, and 74 hours (Table 10). (Right) pyrite rim (white) on grain of pyrrhotite (gray) formed during the slow cooling (1 hour) of a run held at 800° C, 335 bars, and 480 hours. (The grooves in the pyrrhotite in the photograph are scratches resulting from polishing.)

the usual quenching techniques. A considerable amount of pyrite developed at the expense of pyrrhotite and liquid, and in polished section the pyrite was observed to rim the pyrrhotite.

Reversibility of the reaction is demonstrated by the formation of pyrite from its components and the decomposition of synthetic pyrite.

TABLE 5

RESULTS OF RUNS IN GOLD TUBES USING VARIOUS STARTING MATERIALS AT A PRESSURE OF 1,000 BARS

T, °C	Time, hrs.	Products	T, °C	Time, hrs.	Products
(a) Synthetic troilite + sulfur					
775	168	Po + S	750	134	Py + trace Po + S
775	0	Py	750	214	Py
	(2.5 heat up)		725	120	Py
(b) Synthetic troilite + sulfur in excess					
775	0	Py + S	750	134	Py + Po + S
	(2.5 heat up)		750	214	Py + S
775	159	Po + S	750	411	Py + Po + S
(c) Synthetic pyrite					
775	0	Py	750	214	Py
	(2.5 heat up)		750	411	Py + Po + S
775	159	Po + S	725	120	Py
750	134	Py			

TABLE 6

RESULTS OF RUNS IN GOLD TUBES USING VARIOUS STARTING MATERIALS AT A PRESSURE OF 2,000 BARS

T, °C	Time, hrs.	Products	T, °C	Time, hrs.	Products
(a) Synthetic troilite + sulfur					
800	140	Po + S	750	62	Py
775	69½	Po + S	700	63	Py
775	96	Po + S			
(b) Synthetic troilite + sulfur in excess					
775	69½	Po + S	750	62	Py + S
775	96	Po + S	700	63	Py + S
760	350	Py + S			
(c) Synthetic pyrite					
800	140	Po + S	760	350	Py
775	69½	Po + S	750	62	Py
775	96	Po + S	700	63	Py

Runs at 1,000 Bars.—The breakdown of pyrite takes place between 750° and 775° C at this pressure (Table 5). In some of the runs at 750° C small amounts of pyrrhotite and sulfur accompany pyrite. All three phases can be in equilibrium only on the univariant reaction curve. The small amounts of Po + S suggest that during the run the temperature reached or exceeded the equilibrium temperature occasionally. The variation in temperature is attributed to variations in temperature regulation. Since the variations are of the order of ± 5° C the equilibrium temperature for this pressure is close to 755° C. The Po + S in the runs at 750° C cannot be

TABLE 7

RESULTS OF RUNS IN GOLD TUBES USING VARIOUS STARTING MATERIALS AT A PRESSURE OF 5,000 BARS

T, °C	Time, hrs.	Products	T, °C	Time, hrs.	Products
(a) Synthetic troilite + sulfur					
900	2	Po + S	825	4	Po + S
850	24	Po + S	800	24	Py + Po + S
(b) Synthetic pyrite					
900	2	Po (n.l.) + S + (Py)	825	4	Po (n.l.) + S + (Py)
850	24	Po (n.l.) + S + (Py)	800	24	Py

(n.l.) = no lamellae; (Py) = pyrite rims and blebs.

attributed to unreacted starting material. The runs quenched immediately after the desired temperature was attained show that the formation of pyrite is complete and no decomposition of already formed pyrite takes place during the period required to heat up the pressure vessel.

Runs at 2,000 Bars and 5,000 Bars.—The equilibrium temperatures appear to lie between 760° and 775° C at 2,000 bars (Table 6) and between 800° and 825° C at 5,000 bars (Table 7).

DESCRIPTION OF PHASES

Pyrite.—A photomicrograph of a representative sample of pyrite, obtained at 725° C, 335 bars, 336 hours, is given in Figure 3. The average

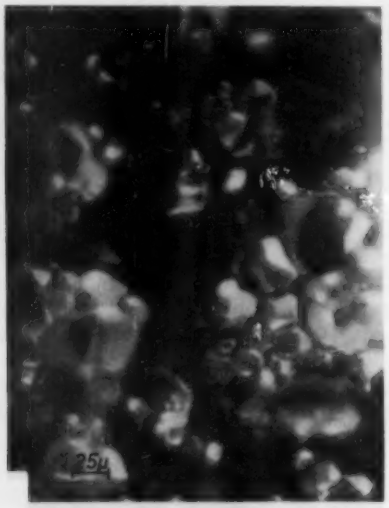

FIG. 3. Photomicrograph of synthetic pyrite crystals grown at 725° C, 335 bars, and 336 hours from synthetic troilite and sulfur in excess.

size of the crystals is less than 10 microns; the largest crystal observed was about 20 microns in diameter. The pyrite is brass yellow when coarse grained and appears black when fine grained. In several experiments in which black pyrite was the starting material small yellow crystals of pyrite were deposited at one end of the gold tube while the starting material remained black. The change in color is attributed to increase in grain size resulting from rapid growth from the gas phase. Pyrite grows as cubes, octahedra, pyritohedra, and dodecahedra. No systematic relationship could be found between crystal habit and conditions of formation. Several forms and intergrowths of these forms were often observed in the same run.

Powder X-ray diffraction studies of crystals from the range of conditions

investigated indicate there was no variation in the unit cell within the limits of error. Using quartz as an internal standard, the unit cell length was found to be 5.419 ± 0.002 Å (Table 8). Within the limits of error this value agrees with those obtained by previous workers on synthetic and natural

TABLE 8

UNIT CELL DIMENSIONS OF SYNTHETIC PYRITE FORMED UNDER VARIOUS CONDITIONS

Tube	T, °C	P, bars	a_0, ±0.002 Å	Tube	T, °C	P, bars	a_0, ±0.002 Å
SiO_2	400	n.d.* (<1)	5.419	Au	725	335	5.420
SiO_2	600	n.d. (<1)	5.421	Au	725	1,000	5.420
SiO_2	700	n.d. (<10)	5.419	Au	750	1,000	5.419
Au	700	2,000	5.419	Au	800	5,000	5.419
							5.419av.

* Not determined.

pyrite (see Table 1). The observed reflections given in Table 9 compare well with those published by Swanson, Gilfrich, and Ugrinic (86).

Pyrite in ore deposits has been found to contain as much as 200 p.p.m. of gold, about 6 ounces per short ton, according to a summary by Fleischer (25). It was important, therefore, to investigate whether or not gold from

TABLE 9

POWDER X-RAY DIFFRACTION DATA FOR A SYNTHETIC PYRITE PREPARED FROM PRECIPITATED FeS_2 HEATED IN A SULFUR ATMOSPHERE AT 700° C FOR 4 HOURS (SWANSON ET AL., 86) AND ONE PREPARED FROM SYNTHETIC TROILITE AND SULFUR IN EXCESS AT 750° C, 1,000 BARS, AND 134 HOURS

hkl	Swanson et al. (86)		Present work		hkl	Swanson et al. (86)		Present work	
	d	I*	d	I*		d	I*	d	I*
111	3.128	36	3.128	38	311	1.633	100	1.634	100
200	2.709	84	2.710	84	222	1.564	14	1.564	18
210	2.424	66	2.424	77	230	1.503	20	1.503	16
211	2.212	52	2.212	52	321	1.445	24	1.448	22
220	1.916	40	1.916	58					
					a_0 (av.)	5.417		5.419 ± 0.002	

* Relative intensity based on arbitrary linear scale.

the tube walls diffused into the pyrite. Dr. O. Joensuu kindly made spectrographic analyses of two samples of pyrite synthesized in gold tubes at 750° C, 2,000 bars, 62 hours (Table 6a). The analyses gave the following results in p.p.m.:

Au	80 ± 10	Ag	1–5
Co	5–10	Cu	100–300
Ni	10–20	Si	100–200
Ti	~30	Mn	~100

Comparison of these results with the analysis given for the iron used in the starting materials (see above) indicates that with the exception of gold the same principal trace elements occur in the iron and pyrite. Some of the gold in the pyrite sample could be attributed perhaps to dust arising from the opening of the tube by filing. Careful examination under the microscope and in polished sections did not reveal any free gold. It is most unlikely that the stability of pyrite would be altered significantly if all of the gold reported in the analysis (80 p.p.m.) were in solid solution. It would be important both theoretically and economically to determine whether or not the gold in natural pyrite is present in solid solution or as free gold.

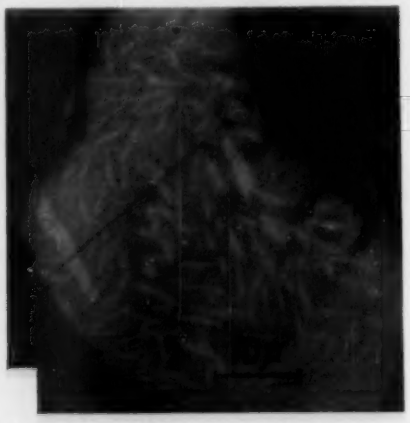

FIG. 4. Photomicrograph of lamellae in pyrrhotite grown from synthetic troilite and an excess of sulfur at 750° C and 23¼ hours under the pressure of the system in a silica glass tube. The lamellae are believed to have formed during the quench and are preserved only if the quench is rapid as described in the text.

Pyrrhotite.—Crystals of pyrrhotite formed with pyrite and a vapor in those experiments carried out in silica tubes (free space small or negligible) below 743° C when the starting materials did not contain sulfur in excess of that in pyrite. Above 743° C pyrrhotite formed in equilibrium with liquid and vapor in silica tubes whether or not sulfur was in excess of that in pyrite. In the gold tube experiments pyrrhotite formed only above the breakdown of pyrite, in equilibrium with a liquid (or gas). Synthetic pyrrhotite is dark gray in color, magnetic, and commonly forms hexagonal prismatic crystals. In polished sections the crystals are cream colored and in some runs exhibited lamellae. The average width of the lamellae shown in Figure 4 is 0.6 micron and they occupy about 24 percent of the area of the section as determined by point-counting. The lamellae are light gray, anisotropic, have a greater reflectivity and hardness than the host pyrrhotite, and are distributed throughout the host along at least three planes. The lamellae appeared in many runs (Tables 3, 10) where pyrrhotite was stable above 743° C. Rapid quenching

was necessary to preserve the lamellae. The quenching procedure described for the steel pressure vessels was not sufficiently fast, and no lamellae were observed in runs made by means of those techniques. It was not possible to observe the lamellae, if present, in runs below 743° C because pyrrhotite was present in only trace amounts when a stable phase.

Pyrrhotite formed as the result of the decomposition of pyrite and quenched to room temperature yields a powder X-ray diffraction pattern different from troilite quenched from temperatures between 550° and 600° C. Troilite exhibits sharp well defined reflections from the (100), (101), (102), and (110) planes, of which (102) shows the highest intensity. On the other hand, pyrrhotite formed on the decomposition of pyrite exhibits broad, diffuse reflections for the same planes, of which (110) may be the most intense, and an additional reflection equal in intensity to that from the (101) reflection sometimes appears at about $d \approx 2.54$. This additional reflection ($d \approx 2.54$) occurs mainly in powder X-ray diffractometer patterns of rapidly quenched pyrrhotites that contain the earlier described lamellae. The $d \approx 2.54$ reflection is attributed to the substance comprising the lamellae and is probably the strongest reflection in the X-ray pattern of the lamellar phase.[4] The broad and diffuse character of the reflections from the (100), (101), (102), and (110) planes of pyrrhotite that has the NiAs structure type is due to the inhomogeneity produced by exsolution of the lamellar phase. The lamellae appear to be related to a rapid inversion which at least for the most iron-deficient pyrrhotites takes place between 650° and 700° C in silica tubes (Kullerud, unpublished data, 1956).[5] It is clear, however, that at and above the temperature of the breakdown of pyrite, pyrrhotite consists of a single, homogeneous phase in equilibrium with liquid and vapor, or gas.

The position of the X-ray reflections from pyrrhotites formed on the incongruent melting of pyrite when compared with those of troilite indicates that iron deficiency causes a contraction of the lattice. Arnold (8) has shown that the composition of pyrrhotite formed below about 665° C can be estimated from $d_{(102)}$. However, the pyrrhotites of the present study, which were rapidly quenched from temperatures above 700° C consist of two phases. At least one of these phases (the NiAs structure type phase) changes composition during the quench. In addition, pyrite forms readily during the quench. One may assume that either the outer portions of the pyrrhotite are converted to pyrite by reaction with the gas without alteration of the core of the grain or pyrite exsolves from the entire grain, or both. Since both rims and blebs were observed (Fig. 2a) it is likely that both processes take place and the sulfur content of the pyrrhotite is therefore underestimated. The values obtained for pyrrhotites examined in polished section are given in Table 10. These runs are supplementary to those given in Tables 3–7

[4] The complete X-ray pattern of the lamellar phase, obtained by means of long exposures in film cameras, is given by Arnold (8).

[5] Apparently similar lamellae have been observed in natural pyrrhotites by van der Veen (92) in 1925, Schneiderhöhn and Ramdohr (78) in 1934, Scholtz (79) in 1936, Ramdohr (69) in 1950, and Vokes (94) in 1957. Hiller and Probsthain (40) present differential thermal analysis data which suggest an inversion at about 620° C, in several natural pyrrhotites.

and were made to test the effect of both pressure and temperature on the composition of pyrrhotite formed as a result of the incongruent melting of pyrite. The apparent composition of pyrrhotite ranges from $Fe_{0.85}S$ in those runs quenched relatively rapidly to $Fe_{0.88}S$ in those runs quenched relatively slowly. The change of composition with quenching procedure is in accord with the shape of the solvus determined by Arnold. Because of the formation of pyrite on quenching and the presence of lamellae, no accurate estimate of the pyrrhotite composition can be made.

TABLE 10

COMPOSITION AFTER QUENCHING OF PYRRHOTITES FORMED ABOVE THE INCONGRUENT MELTING OF PYRITE USING THE ARNOLD $d_{(102)}$ VS. COMPOSITION CURVE. STARTING MATERIAL WAS TROILITE + SULFUR EXCEPT AS INDICATED.

T, °C	Time, hrs.	Deg. 2θ $\pm 0.02°$ (CuKα)	Mol. percent Fe	Remarks	T, °C	Time, hrs.	Deg. 2θ $\pm 0.02°$ (CuKα)	Mol. percent Fe	Remarks
5,000 bars									
900	2	44.02	46.60		825	4	44.00	46.67	
A 850	24	44.01	46.63						
2,000 bars									
850	74	44.02	46.60	n.l.; (Py)	850	74	44.01	46.63	n.l.; (Py)
1,000 bars									
850	74	44.00	46.67	n.l.; (Py)	850	46	44.01	46.63	n.l.
850	74	44.01	46.63	n.l.; (Py)	850	46	44.00	46.67	n.l.; (Py)
500 bars									
850	118	44.00	46.67	n.l.; (Py)	850	118	43.99	46.70	n.l.; (Py)
Open gold tube in silica tube									
B 850	151	44.19	46.00	lamellae; (Py)					
Sealed gold tube in silica tube with sulfur									
850	188	44.21	45.94	lamellae; (Py)					
Silica tube									
850	120	44.18	46.07	lamellae; (Py)	C 760	235	43.54	45.88	lamellae; (Py)
850	150	44.20	45.97	lamellae; (Py)	760	235	43.54	45.88	lamellae; (Py)
C 760	235	43.54	45.88	lamellae; (Py)	A 746	24	44.22	45.95	

A. Synthetic pyrite; B. Troilite + sulfur in excess; C. Natural pyrite, Sulitjelma, Norway; n.l. = no lamellae; (Py) = pyrite rims and blebs.

TABLE 11

POWDER X-RAY DIFFRACTION DATA FOR ORTHORHOMBIC SULFUR

hkl	M. I. Cook (unpublished data, 1957)		Present work		hkl	M. I. Cook (unpublished data, 1957)		Present work	
	d	*I*	*d*	*I*		*d*	*I*	*d*	*I*
111	7.72	9	7.72	6	026	3.450	42	3.452	42
113	5.77	17	5.76	11	224	3.387	4	n.o.	
022	5.70	11	5.69	7	311	3.338	23	3.337	29
202	4.81	4	n.o.		040	3.220	49	3.218	30
115	4.19	5	4.20	4	313	3.115	26	3.112	24
220	4.06	15	4.08	16	008	3.085	15	3.076	14
131	3.92	20	3.94	21	044	2.848	23	2.847	22
222	3.858	100	3.871	100	331	2.670	3	2.670	7
133	3.571	11	3.582	11					

n.o. = not observed.

The gold content of synthetic pyrrhotite was not determined. Natural pyrrhotite contains much less gold than is found in pyrite (25, p. 1009).

Sulfur.—When the liquid, vapor, or gas[6] in equilibrium with pyrite, pyrrhotite, or both is quenched, crystals of sulfur are formed. The crystals may be disseminated throughout or coat the sulfide crystals, congregate in lumps or masses at one end of the tube, coat the wall of the tube, or form botryoidal masses throughout the charge. The color of the liquid observed at temperature through the wall of the silica glass tubes was dark brown at 725° C, greenish brown at 742° C, and dark green at 750° C. On crystallizing, the material turned yellow, yellow with a green tint, and greenish yellow, respectively. The color of the sulfur is also dependent on the length of run as well as the temperature. The green color of the sulfur became darker as the length of run increased up to about 5 hours. No further change was observed after 5 hours. The green color is believed to be a function of the iron content of the liquid. It appears as though the liquid may also change structure as well as composition with temperature. Several molecular species have been identified in sulfur liquids (10). The gas quenched in the gold tubes was white to yellow when observed at room temperature.

Powder X-ray diffraction patterns made at room temperature of the sulfur showed that it was the orthorhombic polymorph. The reflections are recorded and compared with those for pure orthorhombic sulfur in Table 11.

Three runs were made to determine the quantity of iron in the liquid. Mixtures of S and FeS in the ratio of 19 to 1 by weight were run at 730°, 742°, and 760° C in silica glass tubes. Crystals of pyrite or pyrrhotite grew

[6] The words "gas" and "vapor" are used as defined by Morey (59, p. 230): Gas is "a noncrystalline phase which expands to fill all the space available." "A vapor is a special case of a gas" which can be condensed to a liquid. These definitions usually refer to unary systems; however, for binary systems the definitions are arbitrary. In the present work the term gas is used to describe the phase which fills the available space at pressures above the critical pressure of pure sulfur. The term vapor is used to describe the gas phase in equilibrium with liquid or which can be condensed to a liquid at the pressure under consideration.

in the melt indicating that the solubility of iron is less than 5 weight percent at these temperatures. In an experiment at 800° C in which pyrrhotite, liquid, and vapor were in equilibrium, the sulfur formed on quenching was removed and heated in air. The ferric oxide remaining after oxidation indicated that less than 0.1 weight percent Fe was present in the liquid. This result is in agreement with the estimates made by Rosenqvist (73, p. 42, footnote; and personal communication, 1956).

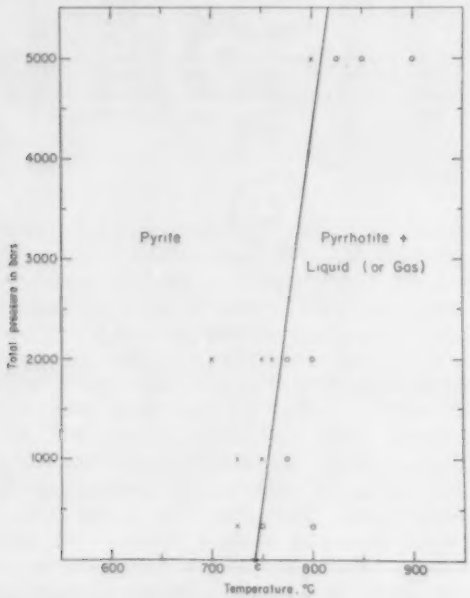

FIG. 5. The determined univariant curve for the reaction $FeS_2 \rightleftharpoons Fe_{1-x}S + L$ which terminates at point *c*, 743° C and approximately 10 bars.

UPPER STABILITY CURVE OF PYRITE

The univariant curve for the reaction $FeS_2 \rightleftharpoons Fe_{1-x}S + L$ [7] derived from the data in Tables 3–7 is shown as a straight line of best fit in Figure 5. The reaction temperature rises at the rate of about 14°/1,000 bars (= 71 bars/°). The temperatures on the line at the pressures investigated are given in Table 12. The error in the temperature at the pressures investigated is less than ± 5° C. The pressure of the point labeled *c*, the lower pressure terminus of the above reaction was not measured; however, an accurate estimate can be

[7] The reaction above the critical pressure of sulfur is by definition $FeS_2 \rightleftharpoons Fe_{1-x}S + G$. No change in phase is implied by arbitrarily changing the name of the phase L (liquid) to G (gas). See footnote 6.

made. Because the argument concerning the pressure of point *c* is vital to an understanding of many sulfide systems, each step is examined in detail.

Condition of Invariancy.—Since the charge and silica rods do not fill all the free space in the rigid silica tube, the phases in equilibrium therein must always include a vapor phase. For temperatures and pressures at which pyrite is stable and for a bulk composition of FeS_2, a small portion of pyrite dissociates to produce a sulfur-rich vapor and consequently a proportionate amount of pyrrhotite. At temperatures above the breakdown of pyrite, the phases in equilibrium are pyrrhotite, liquid, and vapor. At precisely the temperature of *c*, 743° C, four phases are in equilibrium: pyrrhotite, pyrite, liquid, and vapor. The compositions of all phases can be represented in the two-component system FeS-S. According to the Phase Rule, four coexisting phases in a two-component system constitute an invariant condition, a condition satisfied at only one pressure and one temperature.

TABLE 12

UNIVARIANT CURVE FOR THE REACTION $FeS_2 \rightleftharpoons Fe_{1-x}S + L$

P, bars	*T*, °C	*P*, bars	*T*, °C
5,000	810	335	748
2,000	770	(10)	743
1,000	755		

Univariant Curves about Invariant Point.—The pressure or temperature can change from the invariant point only if one or more phases are consumed, and the system then becomes univariant or multivariant, respectively. If one each of the different phases is consumed in turn, four univariant curves will originate from the invariant point. The three phases in equilibrium along the univariant curves may be described, each curve being specified by the phase (enclosed in parentheses) that is absent.

$$(L) \quad Py \rightleftharpoons Po + V$$
$$(V) \quad Py \rightleftharpoons Po + L$$
$$(Py) \quad Po + V \rightleftharpoons L$$
$$(Po) \quad Py + V \rightleftharpoons L$$

The sequence of the curves about the invariant point may be deduced from the principles of Morey and Williamson (61) and the Morey-Schreinemakers' coincidence theorem (69, p. 246), and the slopes of the curves may be estimated from general considerations of the entropy and volume relations of the various phases. The curves so derived are shown in Figure 6. The two-phase assemblages in the divariant regions between the univariant curves are deduced by considering the permissible phases which will account for all possible compositions in the two-component system. The "composition bar" inset in the divariant regions of Figure 6 is a convenient device for recording the possible assemblages for the complete range of bulk composition.

Method of Obtaining Pressure at Invariant Point.—It can be seen from Figure 6 that, if portions of any two curves about the invariant point are

known, their point of intersection, the invariant point, may be ascertained by projection of the known portions. The data for one of the curves, (V), were obtained in the present work and are given in Figure 5. Data on the curve (L), Py $\rightleftharpoons$ Po + V, have been published by several investigators and their results will now be examined.

Published Data on Py $\rightleftharpoons$ Po + V.—Allen and Lombard (5) obtained data on the curve (L) by means of a method wherein the dissociation pressure of natural pyrite is balanced by the vapor pressure over liquid sulfur. The pyrite and sulfur are held and heated separately in evacuated glass bulbs

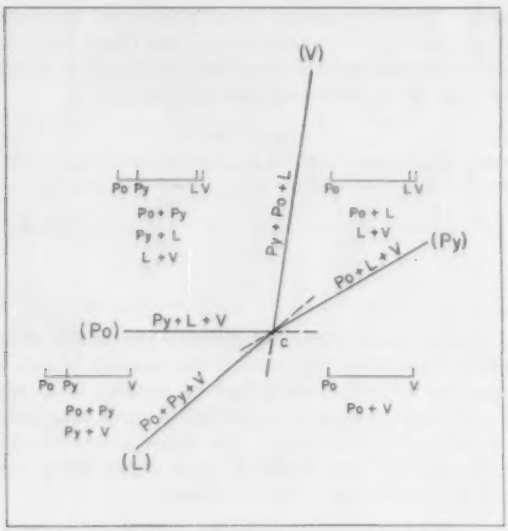

FIG. 6. Univariant curves and divariant regions about point *c* where pyrrhotite, pyrite, liquid, and vapor are in equilibrium. Deduced from thermodynamic principles.

connected by a tube. The temperature of the bulb containing sulfur is adjusted until the pressure in the system is equal to that of pyrite at some higher temperature. If the temperature in the sulfur-containing bulb is too high and consequently the pressure of the system is too high, the pyrite remains unchanged or the breakdown products react to form pyrite. If the temperature of the sulfur-containing bulb is too low and consequently the pressure of the system is too low, the pyrite breaks down or the dissociation products remain unchanged in kind. In this way the pressures along the curve (L), Po + Py + V, may be estimated assuming that the vapor over the liquid sulfur remains pure sulfur during the run. Allen and Lombard used the pure sulfur vapor pressure data given by Bodenstein (13) in 1899, Matthies (55) in 1906, and Ruff and Graf (76) in 1908. The effect of iron on

the vapor pressure of sulfur is discussed below. The dissociation curve of pyrite determined up to 680° C given by Allen and Lombard is shown in Figure 7. The data are expressed in a log P vs. $1/T$ plot in accordance with the integrated Clausius-Clapeyron equation and thereby extrapolated to 743° C.

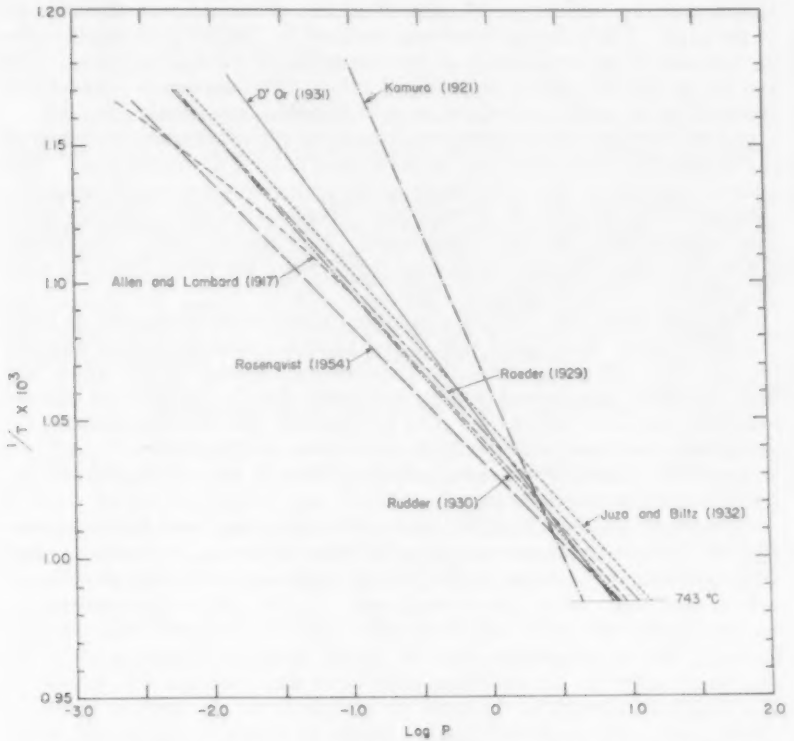

FIG. 7. Summary of data by various workers for $Py \rightleftharpoons Po + V$ on a log P vs. $1/T$ plot. The curves are extrapolated from the conditions investigated by means of the integrated Clausius-Clapeyron equation to 1,016° K (= 743° C), the temperature of the invariant point c where pyrrhotite, pyrite, liquid, and vapor are in equilibrium.

Kamura (47) in 1921 attempted to measure the dissociation pressure of pyrite using a mercurial manometer. The details of his apparatus were not given. Since sulfur reacts with mercury even at room temperature to form HgS, the pressure readings are probably not reliable (Fig. 7).

Raeder (68) in 1929 used a heating curve method described by Hedvall (37, 38) wherein a glass tube containing a natural pyrite sample is heated

at a constant rate. The attenuation of the heating curve is taken as the breakdown of pyrite. The total pressure (< 1 atm.) was adjusted by partial evacuation of the sample tube connected to a large reservoir outside the furnace. The oxidation of the charge by the air remaining in the tube was observed to be negligible; therefore, an inert gas was not used. The pressure in the reservoir was measured by a McLeod gage. Raeder (68) did not believe that the "sulfur vapor" came in contact or reacted with the mercury in the gage. The sulfur pressure was assumed by Raeder to be equal to the air pressure at the temperature of the attenuation of the heating curve. The validity of this assumption is discussed below. The agreement between the results of Allen and Lombard and those of Raeder is remarkable (Fig. 7).

In 1931 D'Or (22) published his results on the dissociation pressures of pyrite using the silica glass spiral of Bodenstein (13) as a pressure gage. The pressure exerted by the sulfur vapor in the evacuated spiral was balanced by air pressure on the exterior of the spiral. The measurement of the air pressure was made by a mercurial manometer. This method gives a direct measure of the sulfur vapor pressure over pyrite along the curve Py + Po + V. The results of D'Or are given in Figure 7.

Juza and Biltz (46) in 1932 constructed a system similar to that of D'Or in which a silica glass spiral with a null point indicator is used to measure the pressure. They measured the pressure over natural pyrite which had been previously decomposed in part, the charge thereby consisting of various ratios of pyrrhotite and pyrite. The pressures at the five temperatures investigated were used to construct the curve given in Figure 7.

In 1936 Rudder (75) used a method similar to that of Raeder and his results are also shown in Figure 7.

A method similar to that of Allen and Lombard was used by Rosenqvist (73) in 1954. He placed a single silica tube containing a mixture of synthetic pyrite and pyrrhotite at one end in a furnace with separate heating coils at each end. With a fixed temperature on the sulfides the temperature was adjusted at the other end of the tube until the dew point was reached. By using the vapor pressure data of A. W. West and Menzies (99) for pure liquid sulfur the decomposition pressure of the sulfide could be estimated. The results of this work on the curve Py + Po + V are also given in Figure 7.

Pressure at Point c.—The curves shown in Figure 7 may be projected as indicated above to 743° C and the pressures read. Neglecting the work of Kamura (47) wherein the sulfur vapor is presumed to be in direct contact with a mercury gage, the range of pressure is 7.2 to 13.5 bars and the average pressure is 10 ± 3 bars at 743° C, point *c*. It is to be noted that this pressure is 12 bars below that of pure sulfur vapor in equilibrium with liquid (Fig. 1). Provided the pressure of 10 ± 3 bars obtained by extrapolation at point *c* is correct, the presence of iron in the vapor is presumed to be responsible for the large decrease in vapor pressure.

Thermodynamic Considerations.—The enthalpy of the reaction (L), Py $\rightleftharpoons$ Po + V, may be calculated by means of the integrated Clausius-Clapeyron equation. The slope of the curves in Figure 7, log P vs. $1/T$, is equal to

TABLE 13

ENTHALPY FOR REACTION Py ⇌ Po + V OBTAINED FROM THE INTEGRATED CLAUSIUS-CLAPEYRON EQUATION USING DATA IN FIGURE 7

Investigator	Enthalpy, Kcal/mol.
Allen and Lombard (5)	80.3*
Kamura (47)	39.0
Raeder (68)	82.9
D'Or (22)	65.9
Juza and Biltz (46)	81.7
Rudder (75)	82.6
Rosenqvist (73)	86.9

* The value was obtained from the linear portion of the curve. The curvature in the low-temperature and low-pressure region is probably the result of errors in measurement. Very small changes in temperature and pressure in this region cause large changes in the slope of the curve.

$-\triangle H/2.303R$, where $\triangle H$ is the enthalpy and R, the gas constant. The enthalpy thus obtained from the data of each investigator is listed in Table 13. The average enthalpy, disregarding the value derived from Kamura's data, is 80 ± 4 Kcal/mol. The enthalpy of the reaction (V), Py ⇌ Po + L, can be obtained by means of the Clapeyron equation, $dT/dP = T\triangle V/\triangle H$. The values of T and dT/dP were determined by experiment; however, the values for the molar volume of the phases are not known.

RELATIONSHIP OF PYRITE IN THE Fe-S SYSTEM

The relationship of the above described reactions involving pyrite can now be described in the light of the Fe-S system. The pressure-temperature diagram for the Fe-S system may be deduced from published data and the new data presented above using the Phase Rule (71, p. 199 ff.). Because of the large pressure range, only a schematic diagram can be presented, although an attempt is made to maintain the temperature scale where possible. The

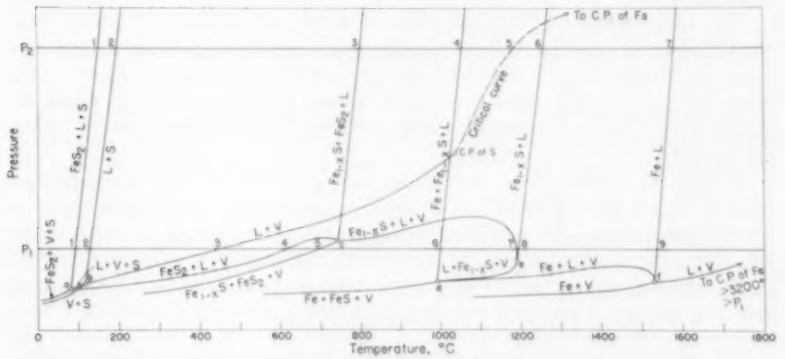

FIG. 8. Schematic pressure-temperature diagram for the Fe–S system. Polymorphic changes have been neglected. The pressure P_1 is approximately 1 bar; P_2, several thousand bars.

details of construction of the P-T diagram shown in Figure 8 are presented in order of increasing temperature. For clarity of presentation polymorphic phase changes have been neglected. In addition, the phases Fe_2S_3 (42), Fe_3S_4 (smythite, 23), and Fe_9S_8 (kansite, 57) have been neglected because their stability fields, if any, are not known with certainty. The pressure P_1 is approximately 1 atm. and P_2 may be considered equal to several thousand atmospheres.

The invariant point *a* is the temperature and pressure at which the four phases $FeS_2 + L + V + S$ [8] coexist; it is the eutectic, "the minimum temperature of liquefaction" (32, p. 462), of the primitive system Fe-S. The four univariant curves originating from *a* can be deduced by means of the principles outlined by Morey and Williamson (61).

One of these curves, labeled $L + V + S$, terminates at the invariant point of pure sulfur, *b*, which has been found by experiment to lie at 115° C and 0.018 mm Hg (89). Point *b* is the triple point of monoclinic sulfur. Portions of the curves $V + S$ (63) and $L + S$ (87, p. 269–275) have been investigated, and the curve $L + V$, which terminates at the critical point of pure sulfur, has been measured in part (99). The boiling point (1 atm.) of sulfur is 444.6° C and the critical point is 1,040° ± 5° C (70) and approximately 118 ± 31 bars according to J. R. West (100).

The curve $FeS_2 + L + V$, for which few experimental data are known to the writers, terminates at the point *c*. Point *c* was found in the present study to be 743° C and about 10 bars. The univariant curves arising from the invariant point *c* were presented in Figure 6. The data for the curve $Fe_{1-x}S + FeS_2 + L$ (Po + Py + L) are given in Figure 5, and those for $Fe_{1-x}S + FeS_2 + V$ (Po + Py + V) are summarized in Figure 7. No data are available for the solubility curve $Fe_{1-x}S + L + V$ except in the vicinity of *e*. The continuation of this curve, $L + Fe_{1-x}S + V$, now a decomposition curve where $Fe_{1-x}S \rightleftharpoons L + V$, terminates at *d*. The phases remain the same; however, the liquid becomes more iron-rich than the crystalline phase.

The temperature of the point *e* was carefully investigated by Jensen (43) and found to be 1,190° C. It marks the congruent melting of the binary compound pyrrhotite, $Fe_{1-x}S$ where *x* is 0.08, under its own vapor pressure.[9] The curve $Fe_{1-x}S + L$ originates at *e* and is tangent to the curve along which the phases $Fe_{1-x}S$, L, and V coexist. No data have been obtained on the curve $Fe_{1-x}S + L$.

Jensen also determined the curve $L + Fe_{1-x}S + V$ and the invariant point *d* where $Fe + L + FeS + V$ are in equilibrium. Point *d* is given as 988° C and the pressure, not determined, is that of the system. The pressure at points *d* and *e* and along the curve $L + Fe_{1-x}S + V$ was believed by Jensen (43, p. 698) to be less than 1 atm. No data are known for the curves $Fe + FeS + V$ and $Fe + Fe_{1-x}S + L$ which originate at *d*. The curve $Fe + L + V$

[8] The phases are arranged in the order of their composition, from the iron-rich first to the most sulfur-rich last.

[9] Pyrrhotite is a binary compound; it melts congruently, but does not exhibit congruent sublimation (crystals $\rightleftharpoons$ vapor) or vaporization (liquid $\rightleftharpoons$ vapor) curves.

has been studied by Friedrich (26, 27) in 1908 and in 1910, Loebe and Becker (54) in 1912, Miyazaki (58) in 1928, and Rosenqvist (73) in 1954.

The point *f* is the triple point of iron where Fe + L + V are in equilibrium. The melting point of iron under 1 atm. of helium is 1,539° C according to Roeser and Wensel (72). The vapor pressure curve of pure iron, Fe + V, has been calculated by Jones, Langmuir, and MacKay (44), and the vapor pressure at the melting temperature is estimated to be about 0.03 mm Hg.

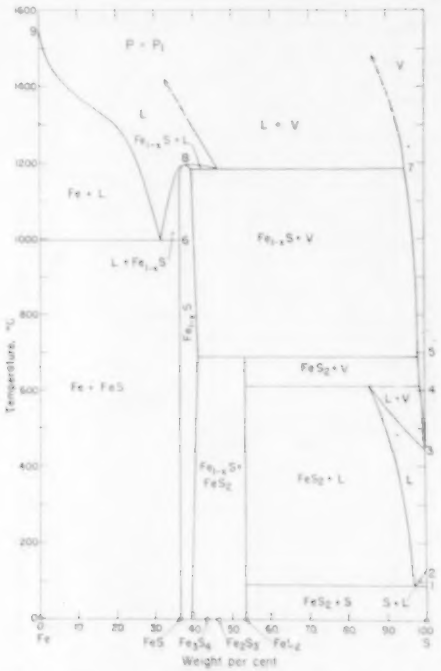

FIG. 9. Schematic temperature-composition diagram for the Fe–S system at the pressure P_1, approximately 1 atm. (see Fig. 8). Polymorphic changes have been neglected, and the solubility of iron in sulfur has been exaggerated for clarity of presentation.

On the basis of these measurements and calculations, the point *f* lies slightly below 1,539° C and about 0.03 mm Hg. The latter authors also give the boiling point of iron as about 3,202° C, and the critical point, therefore, must lie at a temperature greater than 3,202° and at a pressure in excess of 1 atm. The critical point of iron, not shown in Figure 8, is joined by the critical curve (dashed) to the critical point of sulfur (C.P. of S).

Further appreciation of the relationships of pyrite in the Fe-S system may be gained by considering two isobaric sections, P_1 and P_2, through the P-T

diagram (Fig. 8). The T-X diagram constructed from Figure 8 is presented in Figure 9 and represents schematically the equilibrium relations that would be observed at a pressure of about 1 atm. The polymorphic inversions have again been neglected and the solubility of iron in sulfur has been exaggerated for clarity of presentation. The numbered points along the line P_1 in Figure 8 may be located on the T-X diagram (Fig. 9). Similarly the schematic T-X diagram of Figure 10 represents the relations at a pressure of several thousand bars, P_2.

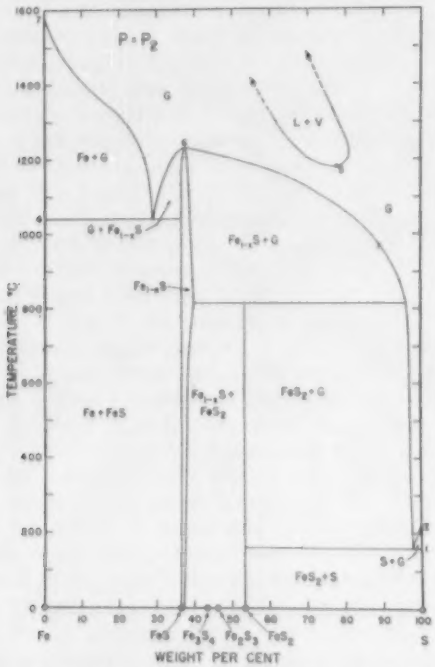

FIG. 10. Schematic temperature-composition diagram for the Fe-S system at the pressure P_2, several thousand bars (see Fig. 8). Polymorphic changes have been neglected, and the solubility of iron in sulfur has been exaggerated for clarity of presentation.

It is important to note that these *sections* at constant pressure differ from the customary *projection* of the so-called "condensed" diagram (see for example Ricci, 71, p. 63) given in Figure 11, wherein the system is under its own pressure and gives only those phases that can exist in equilibrium with a vapor phase. The term "condensed" is, therefore, a misnomer, especially in systems containing volatile components, since vapor is present even though it is neglected. A truly condensed diagram would be one for which vapor (or gas) is absent for all assemblages.

The diagram of Figure 11 is produced by projecting onto the T-X plane those curves in Figure 8 that contain a vapor phase. The lettered points correspond to the invariant or singular points in the P-T diagram. The pressure is variable, and is fixed at a given temperature only when two phases in addition to vapor are present as given by the three-phase curves in the binary system. When only one or two phases are present the pressure is indeterminate unless the volume of the binary system is specified.

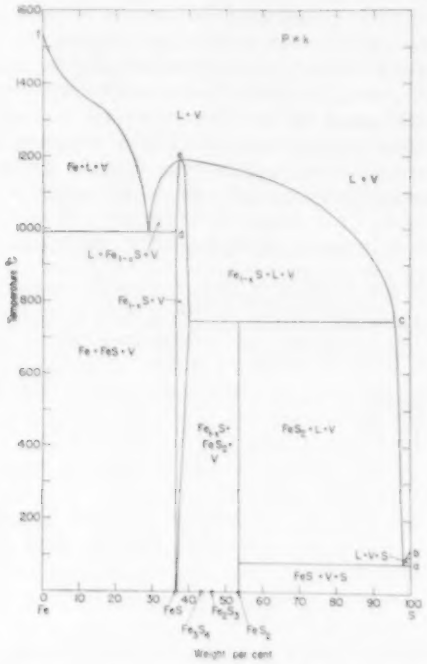

FIG. 11. The so-called "condensed" diagram of the system Fe–S. Vapor is present in all assemblages, and the pressure of the system is not constant.

PREVIOUS CONCEPTIONS OF THE Fe-S SYSTEM

The first attempt known to the writers to construct the Fe-S system was undertaken by Hansen (34, p. 726) in 1936. The relations were given for a pressure of 1 atm. and were for the most part similar to those in Figure 9. Jensen (43) in 1942 constructed a portion of the Fe-S diagram in the region 30 to 50 percent sulfur. On the basis of a single experiment using a natural pyrite Jensen concluded that pyrite melts congruently (p. 705) under the vapor pressure of the system (> 1 atm.). He predicted that pyrrhotite and pyrite would form a eutectic at about 46 weight percent sulfur and 1,000° C

(p. 707). Rosenqvist (73) in 1954 gave a diagram based on Hansen's compilation and incorporated the changes suggested by Jensen. However, he noted that his own work indicated that "pyrite would undergo a peritectic decomposition to give pyrrhotite and liquid sulphur" at about 800° C and 25 atm. The present work resolves this conflict and the initial diagram of Hansen closely represents the relations at 1 atm. (Fig. 9), and the relations under the pressure of the system, i.e., the "condensed" system, sought by Jensen and Rosenqvist are more nearly represented by Figure 11.

Rosenqvist (78, p. 43) raised the question as to "whether a region of liquid immiscibility exists between iron sulfide and sulphur, or whether the two melts are completely miscible." It is presumed that Rosenqvist is referring to the L + V region in the so-called "condensed" diagram (Fig. 11) which on quenching would appear as two intermixed yet distinct crystalline complexes. The products quenched from the L + V region in Figures 9 and 10 might also be mistakenly interpreted as "two melts." To the best knowledge of the writers there is no evidence for a two-liquid region in the Fe-S system.

ANALYSIS OF EXPERIMENTAL METHODS

With the aid of the projections and sections discussed above the nature of the various types of experiments employed may be elucidated.

Rigid Tube.—The evacuated, rigid, silica-glass tube is the container most commonly used for systems involving sulfur. Since the tube is rigid (essentially of constant volume) and free space is available, a vapor phase is always present. For this reason the rigid tube experiments can yield only data that pertain, for example, to a diagram of the type given in Figure 11, the so-called "condensed" diagram. The pressure is usually unknown and is limited by the strength of the heated tube. The tube may be supported by an external pressure in some applications in order to increase its usable pressure range. It should be emphasized that the rigid tube experiments, regardless of an external supporting pressure, cannot yield data for those reactions in which vapor is absent, as the curve in Figure 5 and the other essentially vertical curves in Figure 8.

Collapsible Tubes.—A second type of experiment employs collapsible gold tubes. Here the walls of the container are deformed by application of an external pressure. The internal pressure is taken equal to the external pressure. If the applied pressure is greater than the vapor pressure of the system, then the vapor is condensed to solid or liquid and no vapor is permissible. On the other hand, if the applied pressure is less than the vapor pressure of the system, then a vapor may exist. By this technique the entire P-T-X space may be investigated, yielding data both in those regions in which vapor or gas is permitted and in those in which it is prohibited. Because of restrictions on the malleability of the metal, the collapsible tube technique is probably not useful below several bars pressure.

Connecting Bulbs.—A third type of experiment used by Allen and Lombard (5) employs two evacuated silica-glass bulbs connected by a tube. Allegedly pure sulfur is maintained at a given temperature in one bulb and its

vapor pressure is therefore presumed to be fixed. In the other bulb the sulfide system to be investigated is held at a series of temperatures. In this way the latter bulb is held at a constant vapor pressure. In a similar way Rosenqvist (73) used two connecting bulbs as mentioned above; however, he depended on the decomposition of the sulfides as a source of sulfur vapor. The temperature of the initially empty bulb was lowered until the dew point of the sulfur vapor was reached. The pressure in both experimental systems is assumed to be that of pure sulfur and is read from the sulfur vapor pressure curve. Rosenqvist (73, footnote, p. 42) specifically notes that iron dissolves in the sulfur liquid and that the vapor pressure would be somewhat less than for pure liquid sulfur. It was estimated in an earlier section that the vapor pressure over the stable assemblage at the invariant point (743° C) is about 10 bars, whereas that over pure liquid sulfur at the same temperature is about 22 bars. Such experiments would, therefore, yield approximate data for those regions in which a vapor is permitted. The regions in which vapor is prohibited could not be studied by this technique. It should be noted that true equilibrium cannot be obtained with regard to all phases in the double-bulb apparatus because of the difference in temperature of the two bulbs.

Spiral Gage.—In a fourth technique the pressure of the system is measured directly by the deflection of a spiral silica-glass tube or by a null method in which the internal pressure is balanced by external gas pressure. Free space exists in the sulfur-containing system, so only those regions in which vapor is permitted can be investigated.

Two or More Gases.—A fifth method of studying sulfide systems makes use of an inert gas or a combination of gases. In one case the sulfide is heated in a bulb connected to a large reservoir bulb containing the inert gas. The pressure may be adjusted in the reservoir by suitable pumps to a fixed value. The experiments are made at essentially constant total pressure and a vapor phase is always present. Account should be taken of the solubility of the inert gas in liquid or solid phases; however, the effect is probably negligible.[10]

In another case, two additional gases such as H_2S and H_2 in a fixed ratio are passed over the sulfide. Using the equilibrium data for the dissociation pressure of H_2S and the reaction of H_2S with iron to form an iron sulfide and H_2, the sulfur pressure can be calculated. All equilibria must therefore involve a vapor phase.

It is seen from this brief review of the principal experimental methods that all regions of the P-T diagram are not accessible to all techniques. Since the compositions of coexisting sulfides in nature may be determined by the presence or absence of a sulfur vapor or gas, it is of paramount importance for understanding the ore-forming process to investigate the complex P-T-X space.

GEOLOGICAL IMPLICATIONS

The limits of stability of pure pyrite are fixed by the two curves in Figure 8, $Fe_{1-x}S + FeS_2 + V$, and $Fe_{1-x}S + FeS_2 + L$. Pyrite may form under pres-

[10] The saturation of water with air lowers its equilibrium temperature of melting only 0.0024° C (96) at 1 atm. total pressure.

sures and temperatures to the left of these experimentally determined curves. Natural pyrites may contain small amounts of Ni or Co, which are known to decrease the range of stability of pyrite to a small extent (Kullerud, unpublished data, 1958). Neglecting the effects of solid solution, the circumstances under which pyrite will appear in a rock of the requisite composition can be deduced from the P-T projection and the T-X sections. Two cases may be examined wherein (1) the pressure is due to the overlying rock load and the vapor or gas pressure is equal to the rock load, and (2) the pressure on the solid phases is equal to the rock load and the gas pressure consists of the sum of the partial pressures of a sulfur-rich vapor and at least one other gas. These cases may be considered in a broad sense similar to the circumstances in an anhydrous sulfide magma and a hydrous sulfide vein, respectively.

$P_S = P_T$.—The critical point of sulfur is about 118 bars, which is equivalent to the rock pressure at a depth of about 0.4 km. Since many rocks and ore deposits in which pyrite forms lie at greater depths, the applicable phase diagram would be of the type given in Figure 10 for $P = P_2$. Pyrite could form as a primary phase on the liquidus only in magmas of almost pure sulfur (see liquidus curve bounding field $FeS_2 + G$). Sulfur flows have been observed, for example, by Watanabe (98) in Japan; however, the complete mineralogy was not described. For less sulfur-rich magmas pyrite could not form as a primary phase on the liquidus, arising at lower temperatures ($< 800°$ C for $P = P_2$) by the reaction of pyrrhotite with gas. If the bulk composition were more sulfur-rich than pyrite, pyrrhotite would be consumed in the reaction. If, on the other hand, the bulk composition were less sulfur-rich than pyrite and more sulfur-rich than pyrrhotite, pyrrhotite + pyrite would be the stable assemblage and the gas would be consumed. The presence or absence of pyrrhotite in a pyrite-bearing assemblage is a function of bulk composition and not temperature as is commonly assumed. Vogt (93) believed that pyrite melted congruently and therefore indicated that pyrite could form directly from a melt giving rise to intrusive pyrite ore bodies. The present data do not support this view.

$P_S < P_T$.—When another gas is present, the system then consists of three or more components. It is expected that there will be some solubility of sulfur in the additional volatile components, so the exact relations must be determined by experiment. It is believed that most natural sulfide deposits were deposited under conditions where $P_S < P_T$, the additional volatile components being most likely H_2O and CO_2. If the solubility of sulfur in the additional volatile component is small, the assemblages can be represented in principle for the most part by the projection given in Figure 11. The boundaries of the various fields will, of course, be influenced by the presence of the other volatile components. Pyrite can form as a primary phase on the liquidus when the sulfur content is exceptionally high. For less sulfur-rich systems pyrite can form only by reaction of pyrrhotite with liquid and vapor. The

presence or absence of pyrrhotite in pyrite assemblages will again depend on the bulk composition.

As an example, one may compare the upper stability curve of pyrite when the partial pressure of sulfur is 0.1 and 1.0 bars with the minimum melting curve of granite (91) and the beginning of melting curves of amphibolite and tholeiitic basalt (103) in the presence of water (Fig. 12). A partial pressure of sulfur equal to 0.1 or 1.0 bars is within the range 1 to 10^{-6} atm. believed possible by Krauskopf (51) in a magmatic gas at 600° with $P_{H_2O} = 1{,}000$ atm. Estimates of the breakdown curves for partial pressures of 0.1 and 1.0

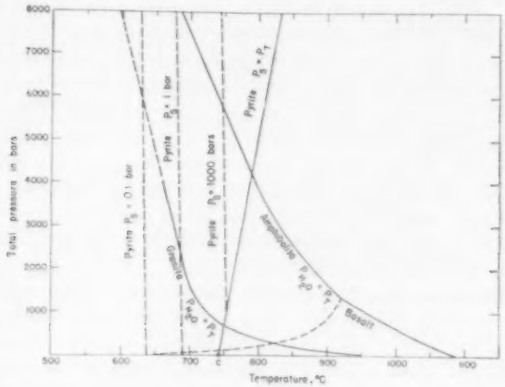

FIG. 12. Calculated upper stability curve of pyrite when the partial pressure of sulfur is 0.1 and 1.0 bar, the estimated upper stability curve of pyrite when the partial pressure of sulfur is 1,000 bars, and the determined upper stability curve of pyrite when the sulfur pressure is the total pressure. These curves are compared with the minimum melting curve of granite (Tuttle and Bowen, 91) and the beginning of melting curves of amphibolite and tholeiitic basalt (Yoder and Tilley, 103) saturated with water when $P_{H_2O} = P_T$.

bars were obtained by calculation using the modified Clapeyron equation (102, p. 515). The following data were used: $\rho_{Fe_{1-x}S} = 4.7$,[11] $\rho_{FeS_2} = 5.0$ giving $\Delta V = 5.3$ cc/mol; $\Delta H = 80$ Kcal/mol (Table 13); and $T = 911°$ and 963° K (5, p. 192) for partial pressures of 0.1 and 1.0 bars, respectively. The dT/dP is found to be approximately $-1.4°$/1,000 bars and $-1.5°$/1,000 bars, respectively.

[11] The densities of various members of the $Fe_{1-x}S$ solid solution series were determined by Hägg (33) and were found to vary from about 4.8 for FeS to 4.5 for an $Fe_{1-x}S$ containing about 54 atomic percent S. By application of the data given by Hägg (33) a density of 4.6–4.7 is derived for the $Fe_{1-x}S$ mix-crystals produced by decomposition of FeS_2 in the present study.

The relations in Figure 12 must, of course, be applied with considerable caution to the field occurrences. The water pressure in rocks is not always equal to the total pressure (102) and the reaction $FeS_2 \rightleftharpoons Fe_{1-x}S + L$ may not be representative in the complex rock system. For these and other reasons the discussion below should be considered only as an expression in principle of possible relations and not a rigorous explanation of field observations.

When the partial pressure of sulfur is 1 bar, pyrite is not stable on the solidus of basalt and could only form near the surface of the earth in basalt at temperatures below about 690° C. On the other hand, pyrrhotite is found commonly in basalt. Pyrite can form on the solidus of amphibolite only above 8,400 bars (= 32 km in depth for rock density of 2.6). Below that total pressure pyrite can form in the solid state at temperatures less than approximately 690° C. In granites, pyrite could form in liquid at pressures above 2,400 bars (= 9 km in depth when $P_S = 1$ bar), and would form only in the solid state below that total pressure at temperatures less than approximately 690° C. Granites formed at moderate to great depths commonly contain primary pyrite; however, primary pyrite is absent in rhyolites. The relations in Figure 12 adequately account for the presence and absence of pyrite in common rocks where the partial pressure of sulfur is very low and the second volatile component is water. It is assumed that small partial pressures of sulfur will not measureably influence the melting relations of basalt and granite in the presence of water.

At partial pressures of sulfur greater than 10 bars (point *c*), the presence or absence of pyrite is determined by a family of curves essentially parallel to those for $P_S = 0.1$ and 1.0 bars rising from the pyrite breakdown curve $P_S = P_T$. Sufficient data are not available to compute the slope of these curves; however, the nature of the curves is represented by the schematic curve for $P_S = 1{,}000$ bars. It is to be noted that changes in partial pressures less than 10 bars greatly affect the upper stability limits of pyrite, whereas partial pressures greater than 10 bars have a much smaller effect on the stability of pyrite. These relationships should be considered with regard to estimates of the temperature of formation of pyrite and of the nature of the ore-forming solution.

The formation of pyrite in sediments involves a more complex system; however, the maximum stability of pyrite will not exceed the curve $Fe_{1-x}S + FeS_2 + V$ in Figure 8. It is seen that pyrite is unstable at very low vapor pressures and pyrrhotite may be expected to form in some sediments. Pyrite is common in many sediments, and authigenic pyrrhotite is rare.

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THE ORIGIN OF HARD HEMATITE IN ITABIRITE

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ABSTRACT

Great confusion exists in the interpretation of field evidence concerning the origin of masses of hard hematite in itabirite. The evidence is briefly reviewed, and some additional observations are recorded. The conclusion reached is that deposits of hard ore in itabirite commonly result from normal weathering processes. Supergene deposits of hard ore are more numerous and more widespread than are deposits of metamorphic or of other modes of origin.

THE presence of lenses and irregular masses of hard, compact, generally blue hematite has been recorded from many deposits of itabirite[1] throughout the World. The genesis of these hard ores has provoked a great deal of discussion, and the field evidence concerning their origin has been interpreted in several different ways. Among the origins suggested, each of the following has received considerable support, and is still currently advocated by its proponents.

1. Syngenetic. The hard ores are original sediments.
2. Weathering.
   a. The hard ores result directly from weathering by the leaching of silica and other impurities, followed by consolidation and reconstitution of the remaining iron.
   b. The hard ores formed by the substitution of iron carried by ordinary ground waters, for silica and carbonate in itabirite.
3. Weathering followed by mild metamorphism. Silica and other impurities are leached by meteoric waters to form soft ores. The hard ores result from mild metamorphism of the soft materials.
4. Regional metamorphism.
   a. The hard ores result from enrichment of the iron caused by leaching of silica and other materials by heated ground waters during periods of regional metamorphism.
   b. The iron carried in heated ground waters replaces silica and other impurities in the itabirite. This is especially operative during periods of regional metamorphism.

[1] Itabirite was defined by Eschewege in 1822 (Geognostisches Gemälde von Brasilien) as the massive, pure iron ore of which the peak of Itabira do Campo, Minas Gerais, Brazil, is composed. Derby (7, p. 817) later used the term to indicate specularite schist. By common usage itabirite is now a synonym for taconite, as used in the Lake Superior region. Much of the rock is schistose, but this is not an essential feature.

5. Magmatic emanations.
   a. The hard ores result from leaching of silica and other impurities by magmatic emanations associated with deep-seated bodies of igneous materials or with lava.
   b. Replacement of silica, carbonates, and other minerals by iron carried in solutions of magmatic origin or affiliation.

Under favorable conditions both iron and silica move readily in either meteoric or magmatic waters, hence broad generalizations about the origin of hard ore are likely to be in error. Each of the listed modes of origin is possible, and probably no two are mutually exclusive. Great confusion exists in the literature, largely because of the complexity of the problems and because of the difference in interpretation of field observations.

The hard ores of the well known districts in Minas Gerais, Brazil, present an interesting example of confusion. Gathmann (16), working in a small area, considered that the hard ores were formed directly from weathering processes by the leaching of silica. He pointed out that tunnels driven beneath hard outcrops encountered soft sandy materials. Harder (23) denied Gathmann's thesis. He thought that the hard ores were continuous in depth. He also emphasized the fact that thin ($\pm$ 2 m) beds of hard ore are continuous along strike for several hundred meters, and are apparently conformable with the enclosing beds. Thin layers of hematite are interbedded with limestones, and structurally the ore beds behave exactly the same as do the nearby sandstone and limestone beds. Harder called attention to numerous outcrops of limestone as evidence that extensive surface solution and decomposition had not been widespread. He believed that the ores are syngenetic, possibly somewhat metamorphosed. A syngenetic origin, followed by mild metamorphism, likewise was proposed by Freyberg (14), by Leith and Harder (31), and by Harder and Chamberlin (22).

Guild (20, 21) considered that the hard ores of Casa de Pedra, in Minas Gerais, were formed by heated waters, possibly of meteoric origin, that ascended along faults. Silica and carbonates were replaced by iron carried in the solutions. Sanders (40) refrained from direct discussion of the origin, but he emphasized the considerable horizontal and vertical extent of the ores. He implied that the Brazilian hard ores are of replacement origin, though he does not say that iron was carried in either hot or cold waters.

Dorr (8, 9) has emphasized that the localization of the Brazilian hard ores was effected by replacement during metamorphism. The migration of iron was apparently controlled by stresses set up during tight folding. Under this theory, hot fluids are thought to have carried iron, and to have migrated from the flanks of folds toward lower energy levels at the crests of folds, where the iron replaced silica and carbonates. Dorr minimizes the effects of surface activities, and he emphasizes hot waters and metamorphism. He states that hard ore alters to powder ore (jacutinga), but does not consider the possibility that powder ore may change to hard ore. In many places in Brazil hard ore changes in depth to jacutinga, and why a crust of hard ore, supposedly formed by hot waters, should be altered by cold meteoric water

to powder ore in depth has not been answered. Isn't the hard ore possibly a type of "case hardening" related to the present or an old surface? Dorr further states (9, p. 296) ". . . many small (1–10 cm thick) hard, pure hematite lenses in itabirite are closely associated with and clearly related to minor quartz veins, indicating the passage of hot waters or gases which could mobilize both the iron and silica." The mere presence of minor quartz veins and hard hematite does not necessarily indicate the passage of either hot water or gases; such veins may be formed by cold water. Emphasis on the lack of quartz veins in either hard or powder ore is also open to question. Locally chert appears to be leached more readily than does crystalline quartz, and in an iron ore deposit in French Equatorial Africa, small quartz veins remain in otherwise high-grade hematite. Eventually both chert and quartz veins are removed by surface leaching.

That replacement is common in the Brazilian hard ores is amply demonstrated by the preservation of the very fine banding typical of itabirite, where minutely crumpled bedding is preserved in great detail. It is difficult to think of hard hematite as being folded in this fashion without resulting destruction of the bedding. Cross-cutting veins of hard blue hematite have also been seen at several places, though they do not appear to be abundant. Other evidence of replacement abounds, and iron has unquestionably been added to itabirite after deformation. At least part of the hard ore was formed by replacement processes, and is not an original sediment. It is likewise difficult to see how hard ore could form by simple leaching of the silica. In this case slump should be recognized, and the overall thickness of the ore bed would probably be less than that of the adjacent beds of itabirite. Slump has not been described by any of the many observers in Brazil, and the ore bodies appear to be at least as thick, and locally thicker, than the nearby beds of itabirite.

The answer as to the origin of the Brazilian hard ores will not be fully known until a thorough study of the geological history and geomorphology has been made. Most geologists who have worked on the deposits in recent years agree that the ores are at least in part of replacement origin. Nevertheless, the necessity of calling upon hot waters to implement this replacement has not been demonstrated. Outcrops of hard ore at both Itabira and at Casa de Pedra seem to be giving way to soft ore and to powder ore as mining becomes deeper. How and why this soft material can be derived by normal weathering processes from an overlying capping of hard ore is difficult to understand. Extensive bodies of hard ore have not yet been found at depths below which supergene agencies are active. Hard ore may possibly have resulted from the action of hot waters, but cold waters may also have been the medium by which iron and silica were rearranged. Ore such as that shown in Figure 1, which contains broken particles of goethite cemented by hard blue crystalline hematite, is difficult to think of as having formed as a result of hydrothermal activities during regional metamorphism.

Similar controversies and confusion exist in regard to most of the other large itabirite or taconite deposits in the World where hard hematite masses

are found. In Venezuela, Alcaino and Ascanio (1) thought that supergene action on iron-rich rocks developed compact masses of hard hematite. The enrichment was effected by a process of substitution rather than by one of leaching alone. Burchard (3) thought that the ores of El Pao were of metamorphic origin, though he was not willing to dismiss the possibility that they were syngenetic. Zuloaga (47) and Zuloaga and Tello (48) thought that the hard ores of the Sierra de Imataca were formed by the reconstitution of itabirite by hot solutions that accompanied granitic intrusions. Lake (30) stated that the ores of Cerro Bolivar were probably syngenetic, combined with partial leaching of the silica.

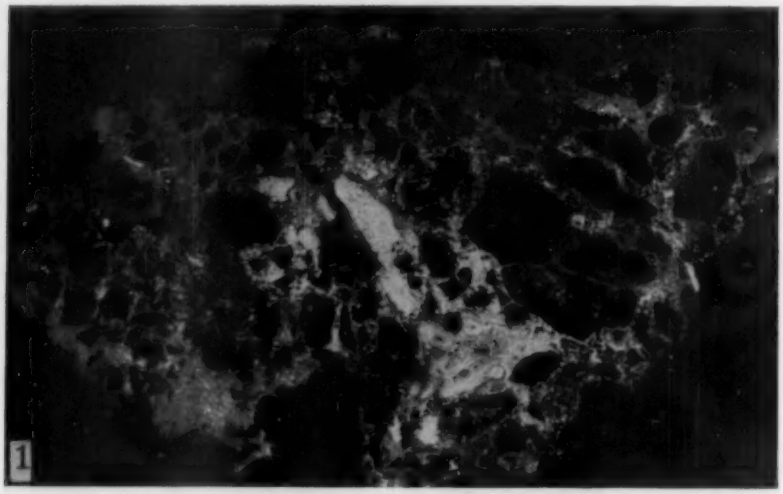

FIG. 1. Photograph of a slab of iron ore from the Angu property, Minas Gerais, Brazil. Clusters of radiating needles of brown goethite are brecciated and recemented by blue hematite. Length of specimen is 8 cm.

In the Lake Superior region the hard ores of the Marquette and Vermilion Ranges have long been considered to be metamorphosed soft ore, as noted by Fulton (15) and Royce (38). The soft ores were formed by leaching of silica and carbonates, either by hot or by cold waters. Roberts and Bartley (36, 37) stated that the ores of Steep Rock Lake, Canada, as well as the hard ores of the Marquette and Vermilion Ranges, were formed by the activity of iron-rich solutions of magmatic origin. This involved the introduction of iron and the replacement of impurities, rather than the simple leaching of silica and carbonates. Schofield (41) suggested that the waters that formed Steep Rock Lake, Marquette Range, and the Vermilion Range, might be heated ground waters rather than waters of magmatic origin. Joliffe (25) remapped the Steep Rock Lake deposit after considerable mining had been done. He

interpreted the ore as an original limonitic sedimentary bed, in part mildly metamorphosed, and with reworking of part of the iron.

Moss (33) described the high-grade ores of Labrador as being secondary, caused by the removal of silica and the addition of iron to a formation that originally contained about 30 percent of iron. Some iron extends into adjacent formations that contained little or no iron originally, thus indicating that much iron has been transported. Moss did not consider it necessary to postulate that hydrothermal solutions played a role in the formation of the iron ore.

In Australia, Lockhart Jack (32) interpreted the hard ores of South Australia as having a hydrothermal replacement origin. Edwards (12), in discussing the ores of the Middleback Ranges, concluded that they might have a hydrothermal replacement origin, but he was inclined to favor a syngenetic origin as being more probable. He thought that a sedimentary origin was favored by the gradation of iron formation into quartzites, by the lack of sulfide in the ore, and by the abrupt and linear character of the Middleback Ranges, which suggest a narrow somewhat intermittent coastal deposit. Later Edwards (13) attributed considerable enrichment to supergene processes. He stated that iron, taken into solution, migrated down dip or down pitch, into structural traps, where it either replaced quartz, or was deposited in voids left by the solution of quartz, in the deeper-lying portions of the banded iron formations. Limonite derived in this manner was converted to hematite before exposure to erosion. Rudd and Miles (39) suggested that the iron ores of the Middleback Ranges formed by removal of silica from the itabirite and enrichment of the iron by supergene solutions. They stated, however, that the ground water is now leaching iron, so the solutions that implemented enrichment differed from the present day ground waters. Similarly, in the Yampi Sound district of Western Australia, Canavan and Edwards (5), considered the ores to be probably of syngenetic origin. Canavan (6) later preferred to consider the ore as an original sediment, though he admitted some evidence to the effect that iron replaced the sediments.

In the Singhbhum district, India, Krishnan (29) favored the replacement of hematite-jasper formation by hydrated ferric oxide, which later became hematite. This was brought about by descending meteoric waters. As supporting evidence Krishnan pointed out that the ore at the surface is hard and compact, but at depth gradually changes to shaly and powdery ores. Dunn (10, 11) thought that early enrichment of the ores resulted from hot waters, but that later enrichment was by cold descending waters. He pointed out that supergene enrichment is going on in India today.

Joubert (27), in discussing the hard ores of South Africa and of South West Africa, considered that thermal action was significant in their formation. At Thabazimbi, in the Rustenburg district of Northwestern Transvaal, he attributed the thermal action to solutions accompanying the Bushveld complex, but at Postmasburg, where no igneous activity is known, he attributed the hard ores to thermal activities during regional metamorphism. His reasons for insisting on thermal activities are not clear. Boardman (2) thought that field evidence indicated that the hard ores at Postmasburg should be

ascribed to prolonged action of weathering agencies. At Thabazimbi, Strauss (43) considered the hard ore to be formed by supergene agencies. Here the hard ore fingers out with increasing depth and grades into ordinary itabirite. It becomes more siliceous and less compact at depth. Tyndale-Biscoe (46) in describing the hard ore deposits in Southern Rhodesia, quoted Swift to the effect that the itabirite beds had been squeezed into a series of lenses. CO_2 and H_2O were driven off by heat, which also converted the limonite into hematite and much of the hematite into magnetite. The silica was redeposited as quartz, and some of the ore was largely desilicified during the metamorphism.

Discussions of this type could be considerably extended, but these few examples suffice to point out the problems of disagreement and confusion concerning the origin of hard hematite ores in itabirite.

SYNGENETIC IRON ORE

The formation of large masses of relatively pure massive hematite by normal sedimentary processes has not been convincingly demonstrated, though it has been advocated by several careful field observers (3, 5, 12, 22). Beds up to 2 meters or more thick, but generally much thinner, such as were described by Harder (23) in Brazil, and which extend along the strike for several hundred meters, are very probably of sedimentary origin. However, many beds of this type contain thin scattered layers of silica or other impurity. They grade into typical itabirite, and commonly they contain diagnostic sedimentary structures and textures. They are usually recognizable as sediments. Where thick, and where composed of relatively pure hematite, the beds commonly show evidence of reconstitution and introduction of iron. It is believed that large masses of hard pure hematite are seldom formed as a direct product of sedimentary processes.

WEATHERING OF IRON FORMATION

The depth of weathering is variable and depends upon many factors, not the least of which is time. Most, if not all, itabirite deposits are Precambrian in age. They are commonly within shield areas where long periods of crustal stability have been favorable for the development of mature topography and deep weathering. Under these conditions, and especially in tropical countries with abundant rainfall, silica is frequently removed to depths as much as 100 meters, and soft sandy itabirite extends to unknown depths, but probably as deep as 500 meters or even more. That iron is transported readily is shown by the development of canga and hard laterite, and by deposition of quantities of limonite where underground waters are exposed to air. The iron apparently travels as a ferrous ion (Fe^{++}) or as finely divided ferric hydroxide. Why, under tropical conditions, iron should be precipitated on the surface as anhydrous hematite rather than as one of the hydrous oxides is not clear, though field evidence confirms the process. Raymond (35) has suggested a possible answer. He showed that the red pigment of many soils in warm, moist regions is hematite. This hematite is not the product of dehydration

of limonite, but probably results from the combined actions of putrefactive and nitrifying bacteria, which could produce ferric nitrate and ammonia. The reaction between these would yield hydrous ferric oxide, which spontaneously loses water and becomes hematite.

FIG. 2. Slab of canga from Minas Gerais, Brazil. Both the fragments and the cement are hematite. The white patches were determined by Kurt Servos as metahalloysite.

Canga is a term widely used in Brazil, and one that is becoming increasingly common elsewhere, especially in the tropics. Unfortunately the term canga, while a useful one, has come to mean different things to different people. Probably the best definition, and one that should be retained, was given by Derby in 1910 (*7*). "Canga is a rock formed by the cementation of hematite of rubble ore into a hard ironstone conglomerate," Figure 2. Custom

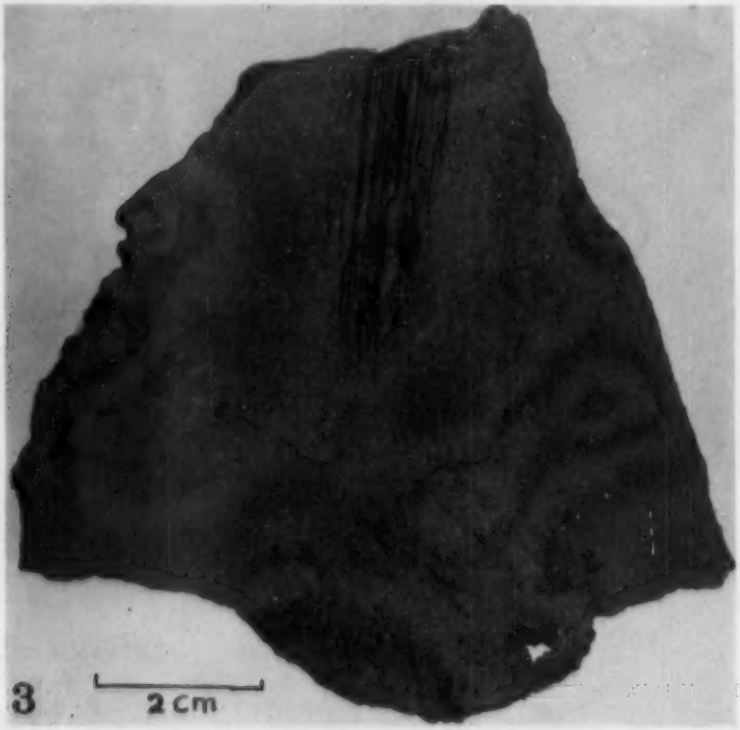

FIG. 3. Photograph of canga slab (hematite), in which the outlines of individual fragments are obscure. The fragments fade into hard ore. French Equatorial Africa.

now includes rubble of limonite ore as well as of hematite. Many fragments in canga are sharply angular; others are sub-rounded to well-rounded. The use of such terms as canga breccia to denote the presence of original angular fragments, is confusing and is undesirable. It should be avoided. Canga grades into hard laterite, and the origins of these two weathering products have many similar features. In places canga cannot be distinguished from laterite. Canga is most abundant in the tropics, where it forms extensive

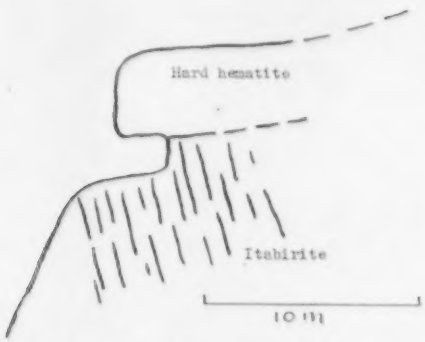

FIG. 4. Sketch of an outcrop of hard hematite ore, showing the relationship between ore and underlying itabirite. Lines in the itabirite are parallel to bedding. French Equatorial Africa.

layers of "pavement," mostly overlying itabirite, but overlapping as well on other rocks. The "pavement" is composed of hard compact hematite, cemented by red or blue hematite, or by limonite. In French Equatorial Africa typical canga grades into hard compact blue ore, Figure 3. This hard ore ordinarily shows no relict fragments, but is in layers on the surface in exactly the same way as the more characteristic canga of Brazil, Figure 4. The conclusion here is inescapable that the hard ore is of supergene origin.

FIG. 5. Photograph of a specimen of ore taken from a surface exposure. Shows crystals of specularite in a vug. The principal material is soft red hematite. French Equatorial Africa. Length of specimen 6 cm.

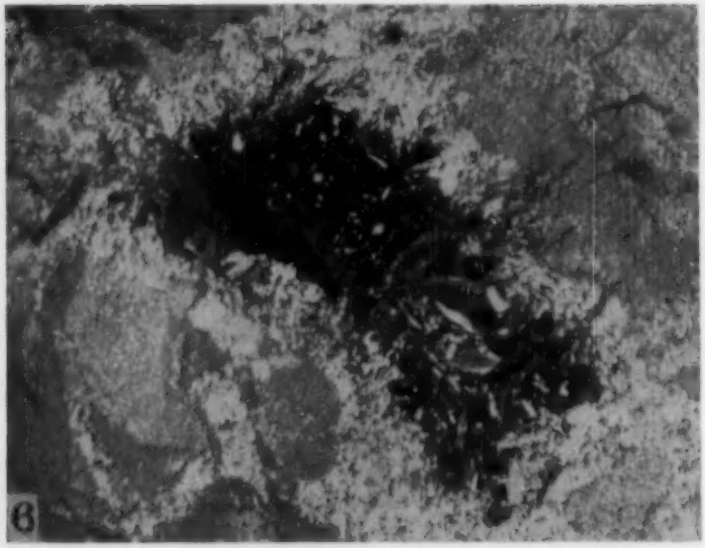

FIG. 6. Same as Fig. 5. Vug showing specularite crystals. Length of vug is 1.0 cm.

Many geologists consider that hematite, and more especially specular hematite, is indicative of hypogene origin—it results from hydrothermal activities. This is based in part upon the presence of specularite in igneous metamorphic and in other unquestioned hydrothermal deposits, and in part upon laboratory experiments (18, 42, 45). Nevertheless, field evidence abundantly indicates that hematite—red, blue, or specular—in itabirite, is very commonly of supergene origin. Figures 5 and 6 are photographs of a specimen of surficial soft red hematite from French Equatorial Africa. This specimen is cut by veinlets of specularite, and contains small vugs lined with specularite crystals. Also in French Equatorial Africa, hard blue hematite, thought to be obviously of supergene origin, is found along joints and water courses in weathered itabirite and in soft red hematite near the surface. Similar seams are found near the borders of weathered dikes, on both walls, but especially along the hanging walls. Possibly conditions existing in a heavy tropical rain forest influence the formation of hematite rather than goethite. Waters near the surface are commonly brown from tannin and organic materials dissolved from decaying vegetation. They are acidic, and in places are reducing. It is believed that, under proper conditions, magnetite as well as hematite is a near-surface product.

Notably absent from most hard ore bodies is evidence of slump, which would be expected if the ores were formed by compaction following leaching

of silica and carbonates. Rather the process near the surface is one of substitution. Iron carried by ground water replaces other materials.

Junner (28), in discussing the hard ore capping in Sierra Leone, thought that ore was formed by action of downward percolating waters on the original schistose hematite and associated rocks. Silica and other soluble constituents were leached, and the remaining material was later cemented by hematite and

FIG. 7. Photograph of a specimen of tightly folded itabirite showing the banded nature of the hematite and silica. French Equatorial Africa.

FIG. 8. Same specimen as Fig. 7. Acetate print brings out the texture of coarsely crystalline hematite, shown as dark patches along the crest of the fold.

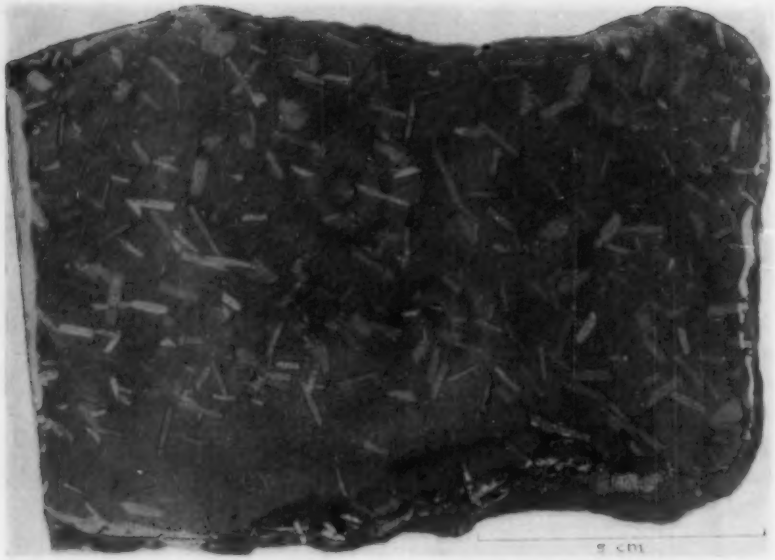

FIG. 9. Polished surface of hard ore from the Andrade mine, Minas Gerais, Brazil. Both the phenocrysts and the groundmass are blue hematite.

limonite. In Sierra Leone, the term lateritic iron ore is apparently a synonym for canga.

The development of hard hematite ore by surface waters under tropical conditions is considered to be a widespread and common process. It is unnecessary to call upon late regional metamorphism or upon hydrothermal fluids to explain hard ore.

HEMATITE FORMED DURING REGIONAL METAMORPHISM

Many geologists favor the theory that hematite is concentrated by heated ground waters during regional metamorphism. Dorr, Guild, and Barbosa (9) pointed out that at Itabira, Minas Gerais, Brazil, ore on the noses of tight folds is generally thicker and of higher grade than is itabirite on the flanks of the folds. This likewise appears to be true at Morro Agudo and at other deposits in Minas Gerais. That the process is entirely possible is convincingly shown in Figures 7 and 8. These figures are of a specimen of tightly folded itabirite from French Equatorial Africa. High grade, coarsely crystalline hematite is concentrated on the nose of the fold. The hard material probably formed in part as a result of substitution and not as a result of leaching of silica. As indicated previously (Figure 1) all of the Brazilian hard ore is probably not formed under hydrothermal conditions. Likewise the specimen of ore from the Andrade mine, Brazil, shown in Figure 9, prob-

ably did not form under conditions induced by tight folding, where both textures and structures would show a strong tendency toward alinement. The specimen is nearly pure hematite, both groundmass and phenocrysts. The crystals, as shown in Figure 9 are vaguely oriented in a northwest direction, though the alinement is probably not rigid enough to have resulted from deepseated metamorphism. The crystal orientation is more likely the result of mild metamorphism, such as might be induced by moderate load.

CONCLUSIONS

The origin of hard hematite in itabirite is a problem of great economic significance, as the deposits formed by weathering will change downward into soft powdery ore and into itabirite. On the other hand deposits formed during regional metamorphism are more likely to continue in depth. In areas such as those of Minas Gerais, Brazil, the depth attained by mining and exploration is insufficient to demonstrate the origin of the ores; they may have been formed by weathering, by migration during regional metamorphism, by hydrothermal fluids working upward along fractures, or by combinations of these features. The fact that the hard ores of Brazil seem to be giving way at depth to powdery ores relates the deposits to similar ones in India, Transvaal, and French Equatorial Africa, where hard materials on the surface finger out downward into powdery ore and into itabirite. These ores are supergene.

Most of the hard hematite ore bodies in itabirite throughout the World fall into two principal classes: 1) those formed by normal weathering processes, and 2) those formed by migration and rearrangement during regional metamorphism. The second class possibly includes some of the hard ore pipes in the eastern United States, though these pipes are not in itabirite, as well as Morro Agudo and others in Brazil. Other deposits, attributed to original sedimentation and to magmatic activities on itabirite, are comparatively of minor significance. A resume of existing evidence indicates that deposits of hard ore resulting from normal weathering processes are probably more numerous and more widespread than are deposits of other types.

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ANOMALOUS LEADS AND THE EMPLACEMENT OF LEAD SULFIDE ORES

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ABSTRACT

In several papers published since 1954 by one of us, suggestions have been made concerning the genesis of a certain class of lead-bearing sulfide orebody of the conformable type. Such deposits are thought to have been derived from seaboard vulcanism and to have been emplaced in off-shore, largely volcanic, sequences, during sedimentation and diagenesis. The metals are considered to have come directly from a deep source—probably the basaltic layer or mantle.

Recently it has been found that the isotope ratios of leads of several such deposits are apparently "ordinary" and extremely uniform, and the leads have suffered no detectable contamination with crustal radiogenic lead. This suggests that they may indeed have come from deep source and that they have been in contact with crustal rocks for no more than a very short time prior to deposition. In contrast the leads of some vein deposits are anomalous and highly irregular, suggesting significant radiogenic contamination. Apparently the leads of the conformable deposits (and some orthomagmatic leads) have been brought to the surface directly from below the continental crust and rapidly isolated and shielded from crustal materials, whereas those of the veins may have spent a considerable time in contact with the latter.

It appears, too, that the occurrence of ordinary and anomalous leads may give important general information on the history of galena-bearing deposits, and that leads from deposits of the conformable type may indicate, with good precision, the age of the sediments enclosing them.

INTRODUCTION

During the last ten years a large literature on lead isotope abundances has developed. Most of it has been concerned with estimating ages—of meteorites, the earth, shield structures and individual rock units. More recently, however, some investigators have begun to consider the geochemical implications of some of the lead isotope assemblages, particularly those now referred to as *ordinary* and *anomalous* leads. Wilson, Russell and Farquhar in Canada, and Cahen, Houtermans and others in Europe have perhaps been the most active in the field and Shaw (12) has recently made an interesting contribution from the geological, as distinct from the physical, point of view.

From work done so far—principally by physicists—it seems that *ordinary* leads may represent direct extraction from great depths in the earth, with *anomalous* leads derived from the ordinary ones by the addition of radiogenic lead in the crust. Thus ores containing ordinary leads are presumed to have come, by igneous activity, directly from below the continental crust and to have been isolated from crustal matter of high radioactivity ever since.

Anomalous leads, on the other hand, must have spent significant time in contact with such crustal materials.

Since 1949, one of us (R. L. S.) has been investigating a number of sulfide deposits of the group referred to as "Conformable" by King and Thompson (8) and has come to the conclusion that at least many of these have been derived from a deep volcanic source and fairly quickly localized in off-reef or equivalent sedimentary facies round volcanic centers. Recently it has been noticed that all the leads from several sampled "conformable" deposits are ordinary, and where a number of specimens from a single occurrence have been analyzed, the isotope ratios are remarkably uniform. In contrast, leads of some vein deposits of the same regions are anomalous and highly irregular in their isotope ratios.

Unfortunately the few isotope measurements so far carried out on conformable orebodies have involved those of which the writers have least geological knowledge; although one of us has made first-hand observations on most of those mentioned in this paper he has not had long experience with them. None has received detailed consideration in the earlier papers and the writers naturally hesitate to pronounce on deposits of which they have comparatively little knowledge and on which experienced mine geologists have worked for many years. All the deposits are conformable, however, and as their lead isotope ratios show common and very distinctive features it seems desirable to draw attention to them and to indicate possible implications. At the same time it must be emphasized that the present ideas are put forward not as a final answer to the problem of conformable deposits, but to indicate a line of investigation that may contribute—possible substantially—to its solution.

In addition to their significance in ore genesis theory, the leads of these conformable deposits may well be of particular importance in dating.

As these ideas should be of interest to many geologists who have not followed recent developments in the field of lead isotope studies (particularly in the physical journals), a brief resume of these is given in the earlier sections of the paper.

THE ISOTOPES OF LEAD AND THEIR DERIVATION

The element lead has four stable isotopes having atomic masses 204, 206, 207, and 208. All four are found in lead extracted from lead minerals in proportions that vary considerably but which might typically be 1.5, 23.5, 22.5 and 52.5 percent, respectively. The proportions of these isotopes can be measured with a mass spectrometer with a precision of a few tenths of one percent of their values.

The atomic weight of lead is sufficiently high that chemical processes occurring in nature do not discriminate significantly between the four masses and therefore cause variations in the observed isotopic proportions. Consequently it is necessary to explain the observed variations in the isotopic composition of lead in another way. It is known that the three heaviest isotopes of lead are identical with those produced by the radioactive decays of uranium-238, uranium-235 and thorium-232, respectively (Fig. 1) and there-

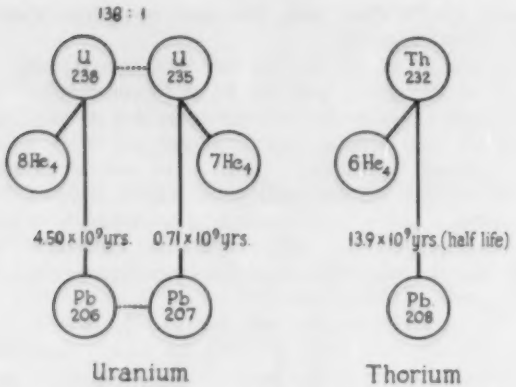

FIG. 1. Schematic diagram showing the production of radiogenic lead isotopes from the radioactive decay of uranium and thorium isotopes.

fore that mixing of lead with uranium-lead or thorium-lead will increase the proportions of lead-206, lead-207, and lead-208 relative to lead-204. Since lead, uranium and thorium occur in the rocks in the outer parts of the earth in comparable amounts, such additions of radiogenic lead might be expected to be usual.

CLASSIFICATION OF LEADS ON THE BASIS OF ISOTOPIC CONSTITUTIONS

Holmes (4) and Houtermans (7) have proposed a model to explain the observed isotope ratios of leads. In essence this model divides the lifetime of any lead sample into two intervals, the first extending for the time (t_o) since the earth first took its present form to the time (t_m) of concentration of lead to form the mineral, and the second extending from the time of formation of the mineral to the present ($t = 0$). It is assumed that in both of these intervals of time the lead from any mineral existed in a closed system, but the second system (i.e., the lead mineral itself) was entirely free of uranium and thorium. It is also assumed that at the initial time (t_o) all terrestrial lead had identical isotope ratios, these ratios being referred to as *primeval*. These simplifying assumptions lead to simple mathematical expressions relating the isotopic constitutions of lead ores to their age and other parameters specifying the time (t_o) and the relative proportions of uranium and thorium in the first of the two systems mentioned above.

Much work has been expended in carrying out isotopic analyses of ore leads and in examining exhaustively the sufficiency of the above assumptions. It is unnecessary to review the details of these researches, for only the broad results are important for the purpose of this paper. It is sufficient to say that this simple theory provides quite a good explanation of the isotope ratios of many ore leads, such leads being referred to as ordinary leads. The model has been used quite successfully as a basis for dating galenas (2, 5, 10, 11).

It is also well known that there are leads whose isotope ratios cannot be explained by this model irrespective of any permissible values chosen for the parameters. These anomalous leads (including samples from Sudbury, Ontario, and Joplin, Missouri) require that their histories be divided into at least three district periods rather than the two required for the ordinary leads. It should be emphasized that this requirement is purely a mathematical result, depending on the nature of the basic equations for radioactive decay, *but is completely independent of any theories of the mechanisms for the formation of lead ores.* The extra period must be inserted between the two previously described for ordinary leads and is often characterized by association of the ordinary lead with large amounts of uranium and thorium.

The existence of both ordinary and anomalous leads is generally accepted, though at present there is no unambiguous method for distinguishing one from the other. There is every probability, in fact, that there is not a clear-cut division at all, and that they simply represent end members of a series of lead types that are anomalous in varying degrees.

One convenient way of circumventing this difficulty is to include among the ordinary leads all those that are not indisputably anomalous. This results in a class of leads that have rather well-defined properties. A suite of such leads representing a single mineralization shows no detectable variation in isotopic constitution. They have isotope abundances that can be explained mathematically by their existence for the first part of their history in a single closed system containing uranium, thorium and lead. The calculated proportions of uranium, thorium, and lead, in this system depend on the particular ore lead considered. The apparent ratios uranium/lead and thorium/lead vary from system to system but are clustered closely about the values of 0.12 atom/atom and 0.47 atom/atom. In fact ratios within about seven percent of those values satisfy the mathematical requirements of essentially all leads of this class. It therefore appears that all these leads have come from source rocks that are all remarkably uniform in uranium, thorium and lead—a fact that is rather difficult to explain in terms of a crustal source because of the extremely variable concentration of these elements in surface rocks. Russell (9) has suggested that the simplest explanation is that true ordinary leads develop in homogeneous materials within the earth's upper mantle and are brought to the surface and formed into minerals at the time of local orogeny. Shaw (12) has pointed out that essentially uniform leads could be produced by mixing, during metamorphism and granitization, of the various leads contained in any heterogeneous sedimentary pile. In this way the crust, as well as the mantle, could provide uniform leads with ratios characteristic of their age. Hence Shaw suggests that it may not be necessary to postulate a subcrustal source. However, if several successive orogenies were considered it is doubtful if such leads would fit a single growth curve, even if sedimentation, metamorphism, and granitization were sufficiently widespread to homogenize the entire crust.

Distinct from the small scatter in the calculated uranium/lead and thorium/lead ratios in the source rocks for the various lead ores is a second sys-

tematic irregularity that has been very difficult to explain. It has been expressed in different ways by different writers, but stated simply the average uranium/lead and thorium/lead ratios apparently increase systematically with the age of the ore. It is evident in Figure 2 as a tendency for the experimental points at the right (young) end of the plot to fall below the predicted growth curve. This effect has been explained at various times as resulting from progressive differentiation of the earth's surface layers, from systematic variations of composition in the earth's surface layers as a function of depth, and from the continual additions of fresh primeval lead from deep in the earth. None of these explanations is very convincing and it is at least as probable that the effect is the result of our inability to distinguish and reject anomalous leads.

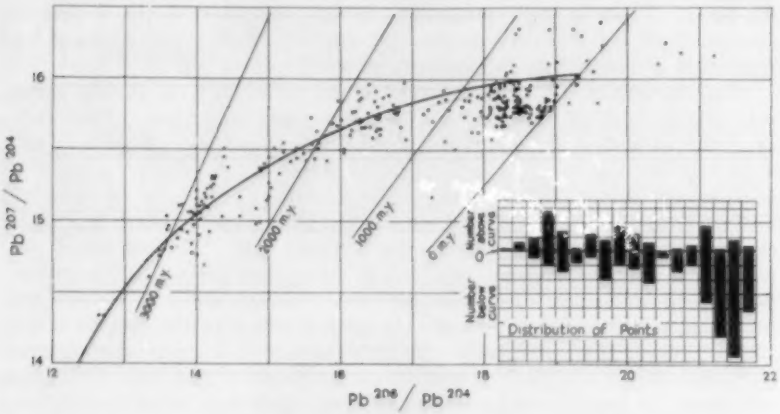

FIG 2. Plot showing measured isotope ratios of common lead samples. About 250 randomly chosen samples are shown.

Anomalous leads themselves have been studied extensively and used to obtain valuable information about the geological age and history of lead ores (10). Detailed analyses of particular deposits show that anomalous leads of a single mineralization have isotope ratios which are linearly related to each other and to some ordinary lead.

The following seem to be the major features of common leads:

1. An ordinary lead is one having isotopic abundances apparently satisfying Holmes' model. This, however, is no guarantee that all such leads have had as simple a history as imagined in obtaining the model.

2. Ordinary leads have apparently all been produced in source rocks remarkably uniform in uranium, thorium, and lead, perhaps implying that they originate well below the continental crust.

3. Anomalous leads require a more complex model for their formation, have variable isotopic constitutions even within single mineralizations and

within a single mineralization have isotopic compositions that are related to each other linearly.

4. Certain of these anomalous leads can be recognized and identified beyond any reasonable doubt.

5. The exclusion of certain anomalous leads from all leads leaves a group having certain small systematic deviations from the simplest forms of Holmes' equations, in which all leads come from a common source material.

If we accept the fact that all leads have been derived from a rather homogeneous source rock, then it is highly probable that both the random fluctuations in isotope ratios about the average curve and the systematic deviations mentioned above result from the use of an unsatisfactory criterion for ordinary leads. It is the purpose of this paper to show that by carefully considering the derivation and mode of emplacement of different lead ore deposits it may be possible to predict precisely a group of leads that should be ordinary and that leads selected from certain conformable deposits deviate from the most simple form of Holmes' model by an order of magnitude less than the deviations that previously obtained using other non-geological criteria.

TYPES OF OCCURRENCE CONSIDERED

For present purposes the following simple division of sulfide deposits is proposed:

1. Deposits of the same age as the enclosing rocks.
   (a) Orthomagmatic deposits
   (b) Sedimentary deposits
2. Deposits younger than the enclosing rocks.
   (a) Fissure fillings (including simple and compound fissures, shear zones, breccia deposits and so on)
   (b) Replacement deposits.

The writers are well aware that this is an oversimplification of what is really a very complex group of categories, and that there is some overlapping between the groupings; it is, however, sufficient for the very general principles now considered. In this "classification," the deposits of 2 (a) are usually easily distinguished, though they may grade into replacement bodies. Those of 1 (a) can usually, though not always (cf. the Sudbury nickel ores), be recognized. Between 1 (b), where the sulfides constitute original particles of the rock, and 2 (b) where they *substitute* for original particles, distinction may be extremely difficult. Clearly the structures, textures and general geological setting of sediments carrying original sulfide on one hand, and those partially replaced by it on the other, should commonly be very similar.

Important among this group of obscure origin are the "conformable" deposits, which seem to be appearing more and more frequently as new mining fields develop and to which class a number of already well-known ore bodies belong. That they might constitute a distinct group was first suggested by King and Thompson (8) in their description of the Broken Hill deposit—an outstanding example of the type. Such deposits characteristically occur

within sediments (commonly volcanic in part), with which they are essentially conformable. Moreover they generally show a distinct preference for one, or a limited number of, units of a sequence, and within these they may prefer an off-reef [1] or equivalent facies. Some of the deposits—Broken Hill, N.S.W.; Mt. Isa, Queensland; Sullivan, British Columbia; Bathurst, New Brunswick—are very large indeed, and there are innumberable smaller ones of the same type. Their marked sedimentary affiliations have led some geologists to propound a sedimentary origin, while others have attributed them to replacement. Many of their features can be explained in terms of either, and their origin has become one of the major general problems of sulfide genesis at the present time.

A compromise has been suggested by Stanton (13, 14) who has pointed out that other rather similar deposits may have formed in a marine environment that has been conducive to sulfate reduction and which at the same time has received unusually abundant supplies of the sulfate itself. Such a situation is thought to have developed in off-reef and equivalent facies in zones of seaboard and submarine vulcanism, particularly along island arcs. It is known that concentration of organic matter—the energy source for sulfate reduction—is greatest along a zone parallel to the coast, and in the off-reef and equivalent facies; in non-volcanic areas, with only normal sea water concentration of sulfate, quite insignificant quantities of sulfide (of the order 3 gm. sulfide per kilogram of sediment) are produced in this environment, but where large quantities of sulfur compounds are contributed by seaboard volcanoes the consequent higher level of sulfate in the near shore waters may increase sulfide production in the bottom muds by many times. It has been suggested that this combination of igneous and sedimentary factors may have lead to the syngenetic development of sediments rich in sulfide, chiefly of iron, which later acted as precipitants for heavy metal halides expelled, principally during compaction and diagenesis, from associated tuff beds.

These alternative theories clearly involve one major difference. If the deposits are sedimentary, or nearly so as suggested by Stanton, they are essentially syngenetic and the metals have not migrated to their present positions through large thicknesses of heterogeneous crustal material. If, on the other hand, they are replacements and hence epigenetic, they have migrated through substantial thicknesses. It is the purpose of the present paper to show how lead isotope abundances may indicate the process involved.

TYPES OF OCCURRENCE AND THE INCIDENCE OF ORDINARY AND ANOMALOUS LEADS

That the isotopic constitutions of ore leads might vary with mode as well as age of deposition has been suspected for some time (1, 10). Houtermans and others (2) have distinguished "J"-type (from Joplin) and "B"-type (from Bleiberg) lead isotope assemblages, both of which they consider to indicate complex histories. Their "J"-type can be recognized by one or more of the following criteria:

[1] Shaley facies to seaward of reef, reef detritus and transitional limestone.

(a) Negative ages.

(b) Discrepancies between the Pb^{206}/Pb^{204} and Pb^{207}/Pb^{204} ratios on one hand and the Pb^{208}/Pb^{204} ratios on the other.

(c) Variation of isotopic ratios of lead in samples from a single occurrence or an area of the same period of mineralization and may have been produced by the addition, during transport, of radiogenic lead.

The "B"-type is characteristically older than the enclosing rocks, and may have been derived, with no additions, from much older deposits—the "rejuvenated" or "secondary hydrothermal" deposits of Schneiderhohn. Recently Russell et al. (10) have noted anomalies of the "J"-type, in a number of orebodies both in Canada and Australia. Although much more confirmatory data is required, it now appears that the occurrence of ordinary and anomalous leads may be ordered, and bear a definite relationship to the type of deposit in which they occur.

Many leads occurring as vein fillings—particularly in Proterozoic or more recent sediments—are anomalous, although many vein leads in basement rocks are not (e.g., Keewatin gold quartz veins). Those of Joplin are now well known, and recent work on vein leads from Broken Hill, N. S. W., Kimberly, B. C., Sudbury and Thunder Bay, Ontario, and elsewhere have shown vein material in sediments to exhibit a strong general tendency to be anomalous. In all cases discrepancies between the different isotope ratios, and large variations in them within single and adjacent occurrences, are characteristic (Table 1).

In contrast to this it has been found that leads from several of the large "conformable" deposits are apparently quite ordinary and, if a number of samples are taken from the one deposit, extremely consistent in their isotope ratios.

In Table 2 are listed eight samples from the Mt. Isa deposit, and seventeen from the conformable orebodies of Broken Hill. In each case the leads are invariably ordinary, and the consistency of the ratios can only be described as striking. Unfortunately only a few results are available for the conformable deposits of Bathurst, N. B., and Sullivan, B. C., but these are quite ordinary and are extremely regular as far as they go. Wanless (personal communication) has recently carried out isotope measurements on a more comprehensive series of galenas from the main Sullivan ore body, and has obtained a similar consistency. In the cases of Broken Hill and Sullivan, the conformable masses on one hand and the vein fillings on the other are neighbouring features, and in each case the first shows ordinary leads with regular ratios, and the second shows anomalous leads with highly variable ratios. In each case the vein leads are distinctly more radiogenic.

In Table 3 are listed analyses of leads from the nickel orebodies of Sudbury, Ontario. These clearly fall into two groups; a less radiogenic one represented by samples 232, 235, 309 and 310, and a more radiogenic one represented by the other samples. The first are ordinary and are fairly regular, and have all come from ore of the main, essentially orthomagmatic Sud-

TABLE 1

ISOTOPIC COMPOSITION OF LEAD FROM VEIN DEPOSITS

No.	Description	204	206	207	208
721	Mayflower Mine, Broken Hill Dist.	1.00	17.91	15.81	38.60
		5.583	100.00	88.29	215.5
722	Mount Robe Mine, Broken Hill Dist.	1.00	19.48	15.91	39.41
		5.134	100.00	81.70	202.3
723	Terrible Dick Mine, Broken Hill Dist.	1.00	18.06	15.83	38.94
		5.536	100.00	87.61	215.6
724	3000 ft. S. of Apollion Mine, Broken Hill Dist.	1.00	18.09	15.83	38.94
		5.529	100.00	87.50	215.3
725	Daydream Mine, Broken Hill Dist.	1.00	17.91	15.78	38.79
		5.585	100.00	88.10	216.6
726	Victory Extended Mine, Broken Hill Dist.	1.00	18.07	15.88	38.97
		5.534	100.00	87.85	215.7
727	Pioneer (Thackaringa) Mine, Broken Hill Dist.	1.00	17.42	15.65	38.12
		5.740	100.00	89.85	218.8
911	Claim on Miner's Lease 165, 17 miles W.S.W. of Broken Hill	1.00	17.38	15.80	38.34
		5.752	100.00	90.86	221.5
415	Joplin I, Missouri	1.00	21.91	16.06	41.32
		4.564	100.00	73.31	188.6
419	Joplin II Electrolytic, Missouri	1.00	22.07	15.99	40.97
		4.532	100.00	72.46	185.7
314	Tri-State District, Missouri:	1.00	21.99	16.12	41.31
	No. 1, Upper Beds, Warsaw fm., Webber Westside	4.548	100.00	73.32	187.8
315	Tri-State District, Missouri:	1.00	22.55	16.14	41.78
	No. 2, Upper Beds, Warsaw fm., Federal Jarrett Mine	4.434	100.00	71.59	185.3
316	Tri-State District, Missouri:	1.00	21.30	16.08	40.78
	No. 3, Veinlet in Chester fm., Diamond Joe Mine, 15′ deep	4.695	100.00	75.50	191.4
317	Tri-State District, Missouri:	1.00	22.64	16.19	41.91
	No. 4, Warsaw fm., Grace B Mine	4.417	100.00	71.51	185.1
318	Tri-State District, Missouri:	1.00	22.04	16.13	41.33
	No. 5, Upper Beds, Warsaw fm., Webber Westside Mine	4.538	100.00	73.18	187.5
319	Tri-State District, Missouri:	1.00	22.64	16.23	41.81
	No. 6, Bed Unknown	4.417	100.00	71.67	184.7
320	Tri-State District, Missouri:	1.00	22.18	16.19	41.51
	No. 7, E Bed, Warsaw fm., Howe Mine	4.507	100.00	72.97	187.1
321	Tri-State District, Missouri:	1.00	22.66	16.20	41.81
	No. 8, K Bed, Keokuk fm., Otis	4.414	100.00	71.51	184.6

TABLE 1—*Continued*

No.	Description	204	206	207	208
322	Tri-State District, Missouri: No. 9, Sheet Ground, O Bed, Keokuk fm., Blue Goose No. 2 Mine	1.00 4.603	21.72 100.00	16.06 73.89	41.05 188.9
323	Tri-State District, Missouri: No. 10, M Bed, Keokuk fm., Blue Goose No. 1 Mine	1.00 4.566	21.90 100.00	16.29 74.36	41.59 189.9
513	Bluebell Mine, British Columbia, Canada	1.00 5.683	17.58 100.00	15.66 88.96	38.27 217.6
860	Bluebell Mine, British Columbia, Canada	1.00 5.744	17.41 100.00	15.40 88.44	37.78 217.0
861	Bluebell Mine, British Columbia, Canada	1.00 5.648	17.71 100.00	15.80 89.26	38.33 216.5
*870	Bluebell Mine, British Columbia, Canada	1.00 5.858	17.07 100.00	15.11 88.48	37.04 217.0
*871	Bluebell Mine, British Columbia, Canada	1.00 5.659	17.67 100.00	15.50 87.71	37.98 214.9
*872	Bluebell Mine, British Columbia, Canada	1.00 5.858	17.07 100.00	15.13 88.65	37.02 216.9
*869	Bluebell Mine, British Columbia, Canada	1.00 5.758	17.37 100.00	15.43 88.84	37.73 217.3
853	Thunder Bay Region: Dorion Mine, Lot 14, Cons. 8 and 9, Ont.	1.00 5.498	18.19 100.00	15.81 86.91	37.78 207.7
475	Thunder Bay Region: North of Dorion, Ont.	1.00 5.391	18.55 100.00	15.95 85.97	37.82 204.8
855	Thunder Bay Region: Silver Mountain, Ont.	1.00 3.327	30.05 100.00	18.26 60.76	41.17 137.0
854	Thunder Bay Region: Ozone Mine, Ont.	1.00 5.458	18.32 100.00	15.89 86.72	37.14 202.7
894	Thunder Bay Region: McTavish Township, Hilma Lake, Ont.	1.00 3.261	30.65 100.00	18.10 59.06	41.45 135.2
892	Thunder Bay Region: McTavish Township, near Pearl Station	1.000 3.256	30.71 100.00	18.21 59.30	41.23 134.3
893	Thunder Bay Region: McTavish Township Lot No. 7, Caribou Mine, Ont.	1.00 2.951	33.88 100.00	18.69 55.17	43.98 129.8
642	Thunder Bay Region: Thunder Bay District Ogama Property, Ont.	1.00 4.827	20.72 100.00	16.40 79.17	38.28 184.7

* These samples were analysed with a different mass spectrometer than were the others.

bury mineralization.[2] The more radiogenic group on the other hand is anomalous and obviously irregular, and as it happens all the samples in this group have been obtained from coarse fillings in young "post-lode" faults.

From all this it appears that:

1. Fissure fillings may contain leads that are more or less anomalous and irregular.

TABLE 2

CONFORMABLE DEPOSITS

No.	Description	204	206	207	208
928	Mount Isa, Queensland, Level No. 11, Coord. 6559N, 1465E, No. 2 Orebody	1.00 6.206	16.11 100.00	15.48 96.08	35.91 223.0
929	Mount Isa, Queensland, Level No. 12, Coord. 7210N, 1745E, No. 5 Orebody	1.00 6.207	16.11 100.00	15.51 96.29	36.12 224.2
930	Mount Isa, Queensland, Level No. 9, Coord. 7405N, 2475E, No. 7 Orebody	1.00 6.204	16.12 100.00	15.55 96.45	36.17 224.4
931	Mount Isa, Queensland, Level No. 9, Coord. 6435N, 2765E, No. 11 Orebody	1.00 6.185	16.17 100.00	15.58 96.34	35.95 222.3
932	Mount Isa, Queensland, Level No. 9, Coord. 8155N, 2455E	1.00 6.215	16.09 100.00	15.53 96.53	36.19 224.9
933	Mount Isa, Queensland, Level No. 1, Sub above 7	1.00 6.226	16.06 100.00	15.50 96.50	36.09 224.7
667	Broken Hill, New South Wales	1.00 6.191	16.15 100.00	15.61 96.64	35.98 222.8
668	Broken Hill, New South Wales, between No. 2 and No. 3 Lenses	1.00 6.186	16.16 100.00	15.61 96.56	35.96 222.4
669	Broken Hill, New South Wales, No. 2 Lens	1.00 6.233	16.04 100.00	15.49 96.56	35.68 222.4
670	Broken Hill, New South Wales, Rhodonitic Zink Lode	1.00 6.225	16.06 100.00	15.49 96.43	35.66 222.0
671	Broken Hill, New South Wales, No. 1 Lens	1.00 6.208	16.11 100.00	15.57 96.64	35.88 222.8
672	Broken Hill, New South Wales, Siliceous Zinc Lode	1.00 6.198	16.13 100.00	15.60 96.68	35.97 222.9
912	Broken Hill, New South Wales, Little Broken Hill Mine	1.00 6.177	16.18 100.00	15.56 96.14	35.89 221.8
913	Broken Hill, New South Wales, Pinnacles Mine	1.00 6.179	16.18 100.00	15.58 96.26	35.92 222.0
914	Broken Hill, New South Wales, Rupee Mine	1.00 6.184	16.17 100.00	15.59 96.39	35.90 221.9

[2] One of us (R. L. S.), in collaboration with Professor J. E. Hawley of Queen's University, has carried out a detailed mineralogical study of the Sudbury ores and considers that all but an insignificant proportion of the sulfides there have formed by solidification from a sulfide melt, and are essentially contemporaneous with the "norite."

TABLE 2—*Continued*

No.	Description	204	206	207	208
915	Broken Hill, New South Wales, Centennial Mine	1.00 6.184	16.17 100.00	15.58 96.30	36.00 222.6
916	Broken Hill, New South Wales, Parnell Mine	1.00 6.154	16.25 100.00	15.69 96.56	36.06 221.9
917	Broken Hill, New South Wales, Balaclava Mine	1.00 6.188	16.16 100.00	15.64 96.73	35.92 222.2
918	Broken Hill, New South Wales, Rising Sun Mine	1.00 6.192	16.14 100.00	15.61 96.73	35.85 222.1
919	Broken Hill, New South Wales, Great Western Mine	1.00 6.213	16.09 100.00	15.53 96.55	36.00 223.8
920	Broken Hill, New South Wales, Globe Mine	1.00 6.183	16.18 100.00	15.65 96.73	35.92 222.0
921	Broken Hill, New South Wales, White Leads Mine	1.00 6.211	16.10 100.00	15.49 96.23	35.49 220.5
922	Broken Hill, New South Wales, Nine Mile Mine	1.00 6.179	16.18 100.00	15.61 96.50	35.71 221.1
807	Bathurst, New Brunswick, Brunswick Mining and Smelting Co.	1.00 5.491	18.21 100.00	15.72 86.29	38.04 208.9
808	Bathurst, New Brunswick, Anacon—Leadbridge Property	1.00 5.440	18.39 100.00	15.86 86.23	38.55 209.6
809	Bathurst, New Brunswick, New Larder U Garland Mines	1.00 5.447	18.36 100.00	15.85 86.32	38.41 209.2
810	Bathurst, New Brunswick, Keymet Mines	1.00 5.447	18.36 100.00	15.81 86.13	38.40 209.2
208	North Star Mine (Nr. Sullivan), British Columbia	1.00 5.937	16.84 100.00	15.86 94.17	36.91 219.1
514	North Star Mine (Nr. Sullivan), British Columbia	1.00 6.034	16.57 100.00	15.64 94.39	36.73 221.6
200	Sullivan Mine, Kimberley, British Columbia	1.00 5.996	16.68 100.00	15.67 93.97	36.59 219.4

2. Conformable orebodies, which may represent either replacement or sedimentation, yield leads that are ordinary and extremely regular.
3. One orthomagmatic deposit has yielded ordinary leads with fairly regular isotope ratios.

GEOLOGICAL PROCESSES AND THE EMPLACEMENT OF ORDINARY AND ANOMALOUS LEADS

If it is assumed that the major proportion of the lead of sulfide deposits comes from a uniform source, and that this source is beneath the continental crust, the systematic occurrence of ordinary and anomalous leads in different types of orebodies can be explained.

The galenas of vein deposits have, *per se*, been deposited in fissures whose existence preceded theirs. Such galenas are therefore younger than the rocks that enclose them and, if the possibility of intense local lateral secretion is ignored, have been derived from a distant source. Moreover, in proceeding from source to site of deposition, a finite thickness of rock is traversed.

TABLE 3

COMPOSITE DEPOSITS, SUDBURY, ONT.

No.	Description	204	206	207	208
211	Worthington Mine	1.00 3.869	25.85 100.00	16.82 65.08	51.86 200.7
217	Garson Mine	1.00 4.403	22.71 100.00	16.48 72.58	44.16 194.3
232	Frood Mine, Coppercliff, 3300 ft. level	1.00 6.334	15.79 100.00	15.63 99.00	36.11 228.7
233	Frood Mine, Coppercliff, 400 ft. level	1.00 4.404	22.71 100.00	16.66 73.37	44.47 195.9
234	Garson Mine (Post Ore Slip)	1.00 4.406	22.70 100.00	16.42 72.33	44.22 194.8
235	Fairbank Township (Quartz veinlet in micropegmatite)	1.00 6.225	15.99 100.00	15.57 97.36	36.52 228.4
307	Hardy Mine	1.00 4.357	22.95 100.00	16.58 72.25	52.07 226.9
306	Falconbridge Mine, 1702—76 Section	1.00 4.184	23.90 100.00	16.76 70.12	45.03 188.4
305	Falconbridge Mine, 2402—22 Section	1.00 4.275	23.39 100.00	16.72 71.46	44.77 191.4
308	Falconbridge Mine, 3302 WD 3A Section	1.00 4.168	23.99 100.00	16.83 70.13	45.16 188.3
309	McKim Mine, 600 Shrinkage	1.00 6.184	16.17 100.00	15.71 97.13	36.43 224.8
310	McKim Mine, 800 ft., 26–28 Shrinkage Stope	1.00 6.218	16.08 100.00	15.65 97.33	36.48 226.8
311	McKim Mine, 1000 E	1.00 4.403	22.71 100.00	16.46 72.46	44.59 196.3
312	McKim Mine, 100′ Below Surface	1.00 4.419	22.63 100.00	16.51 72.95	44.41 196.2

It is known that all crustal rocks, and many sediments in particular, contain uranium, thorium, and radiogenic lead, the quantities and proportions of the three varying from one rock unit to another with corresponding irregularity in lead isotope abundances. Apart from occasional coincidences, such abundances quite naturally may be different from those of the main lead source at depth—processes of erosion, transport and deposition undoubtedly

change original balances of the uranium, thorium, and lead, with consequent local variation of isotope ratios.

Where lead is expelled from a uniform source and commences upward migration, it may be assumed that the transporting medium remains undersaturated with respect to it until the instant of deposition. Further, because of their high atomic weight and the very small proportional differences in weight between them, no fractionation of the isotopes should take place during movement. Because of these factors, the transporting medium should be capable of collecting any lead, radiogenic or otherwise, encountered prior to commencement of deposition. Hence, depending on:

(a) distance from source to site of deposition
(b) duration of transit and
(c) composition and age (hence radiogenic lead content), and thickness of individual rock units traversed

varying quantities of radiogenic lead would be added to the original lead being transported. As, apart from occasional coincidences, the lead/uranium/thorium ratios in the crustal rocks would be different from those in the source, the lead in the resultant galenas would become anomalous. Further, owing to inevitable variation in channels followed by the migrating lead, the amounts of radiogenic material acquired *en route* would vary, and so the resulting ratios would be irregular in consequence. Thus all leads which have travelled finite distances through sedimentary rocks or their derivatives are potentially anomalous. This anomalous quality should be a general characteristic of vein and replacement galenas, and should be recognizable provided that sufficiently precise mass spectrometer measurements can be made.

Conversely, it is only those leads that have not traversed crustal rocks that should be truly ordinary. The only galenas that satisfy this requirement are, of course, those formed at the same time as the rocks that enclose them, viz.:

1. Orthomagmatic deposits in mafic rocks derived from beneath the continental crust.
2. Sedimentary deposits derived from the depth by basalt-andesite vulcanism along, or at some distance from continental margins, and quickly isolated in volcanic sediments.

As both have only the most limited contact with crustal rocks, neither would suffer significant radiogenic contamination of their constituent leads.

It has already been pointed out that anomalous leads with irregular ratios have generally been found in crustal sediments, whereas a number of conformable deposits and one orthomagmatic deposit show ordinary leads with extremely uniform ratios. The inference is now that the leads of the first have migrated through rocks bearing abundant radiogenic lead whereas those of the other types have not.

DISCUSSION

This relationship between lead type and mode of occurrence appears to have fundamental implications both in sulfide genesis and in age determination.

If all lead isotope analyses are plotted as in Figure 2, a fairly systematic, though somewhat diffuse, distribution appears. The points lie about a curve as shown, though the scatter is broad with a heavy development of points beneath the curve as age decreases. Had each of these leads been derived at different times from the same uniform source and if, after separation, each had received no radiogenic addition, all should have fallen on a single growth curve. This they plainly do not do, indicating that at least many of them are not likely ordinary.

In contrast, leads from a number of conformable ore bodies do fit a single growth curve (i.e., a single uranium-thorium-lead system)—and this to within a few tenths of one percent. Unfortunately isotope measurements have been done for only a few of these deposits, but those available have been plotted in Figures 3 and 4; in several cases a single point represents the average of a

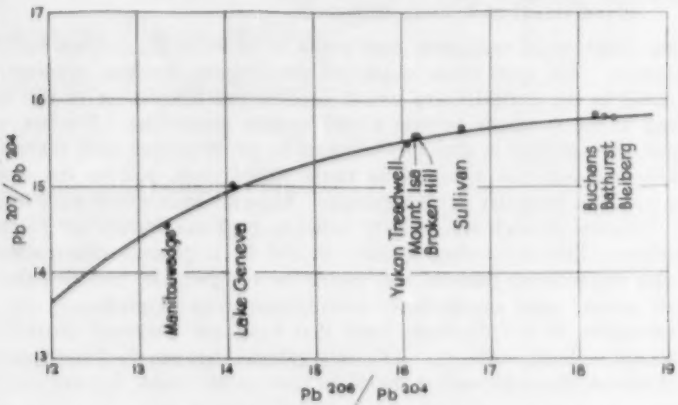

FIG. 3. A similar plot to that shown in Figure 2, but restricted to analyses for lead samples for conformable deposits of the type described in the text. Nine locations are shown, representing more than forty analyses.

number of very regular results, as in the case of Broken Hill. The remarkable consistency between Pb^{206}/Pb^{204} and Pb^{207}/Pb^{204} on one hand and Pb^{208}/Pb^{204} on the other is quite a striking feature. From this several important deductions may be made:

It appears that the deposits of this group are in fact composed of material expelled from a very uniform source during successive periods, that they have been deposited without significant contamination with highly radiogenic lead, and that they represent the source lead at the time of separation. In view of this, their lead cannot have been in contact with older crustal material containing radiogenic lead. This is in accord with the mechanism of derivation and concentration deduced from geological evidence—i.e., that the lead has been derived from the mantle, expelled through volcanoes and either quickly precipitated as sulfide on the sea floor or expelled during diagenesis from associated tuff beds and localized in adjacent iron sulfide-rich sediments (13, 14).

Although, in general, epigenetic leads should be suspected of being anomalous, and certain syngenetic leads should be ordinary and regular, it must be pointed out that there will be many cases which are intermediate to these extremes. While some epigenetic leads will be distinctly anomalous, degrees of this must be expected depending on the vagaries of migration, and while most leads derived simply from a mantle or deep basaltic source should be ordinary, conditions of actual deposition may sometimes cause slight deviations.

Russell et al. (10) have shown that anomalous vein leads of a single mineralization have isotope ratios linearly related to each other and to some ordinary lead (either known or inferred); the anomalous leads apparently

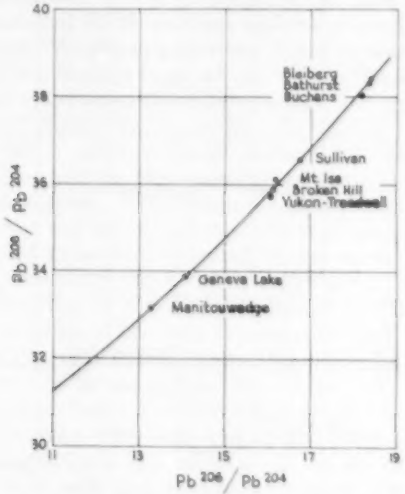

FIG. 4. A plot showing the relationship between the ratios Pb^{208}/Pb^{204} and Pb^{206}/Pb^{204}. The inclusion of Bleiberg in both Figures 3 and 4 may be questioned, as discussed in the text.

having been derived from the ordinary lead by addition of radiogenic matter. In Figure 5 the growth curve of the leads of the conformable orebodies is shown in relation to the anomalous vein leads of Broken Hill, Sudbury and Thunder Bay—in each case the linear plot is tangent to the growth curve, and it is close to this that the least anomalous lead of each mineralization falls. This seems to confirm in a most elegant way the suggestion that the conformable leads represent uncontaminated mantle material, and that anomalous leads develop from the latter by the linear addition of crustal radiogenic lead.

It has already been stated that degree of anomalousness of epigenetic leads would be expected to be related to the nature and thickness of rocks traversed and the time taken in transit. The first of these—the nature of the rocks through which the lead-bearing solutions pass—is perhaps the most important factor of the three. Many sediments particularly, contain notable

quantities of radiogenic matter and in general leads migrating through them would be expected to become anomalous to an obvious degree. On the other hand leads migrating through not long deposited basalt-andesite tuffs would not be expected to suffer much contamination, and the same would hold for many of the leads of major mafic lava terrains.

Illustration of this latter point seems to be provided by some of the work of Russell and others who, working on vein galenas from the Precambrian and Grenville terrains of Canada, have found both ordinary and anomalous types. It has been found, however, that the different leads occur in a pattern

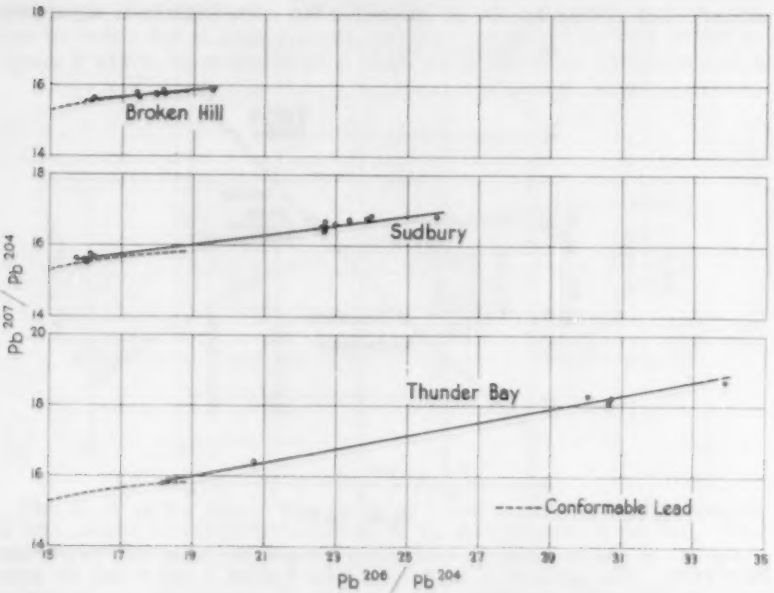

FIG. 5. A plot showing the relationship of suites of anomalous leads to the locus of the conformable leads drawn in Figure 3.

and that, in fact, it can sometimes be predicted in advance whether a given lead will be anomalous or ordinary. Thus those occurring in Eastern Canada in the Keewatin or Timiskaming basement are generally ordinary, whereas those occurring in the Huronian or other Proterozoic-type cover rocks are commonly anomalous.

The reason for this may be as follows. The older terrain consists predominantly of mafic lava, together with smaller quantities of fragmental associates—tuffs or agglomerates—and some sedimentary derivatives. Thus wherever the associated leads have come from, they have had to traverse only material derived from a deep and comparatively uniform source. It has been

pointed out by various workers that many of the gold veins containing the measured galenas are related to later porphyries, but it has been shown by Holmes (6) and Evans (3) that these are simply reconstituted phases of the old volcanic rocks. It is even possible that the galenas in question have been secreted into fissures, and concentrated, from the lavas themselves during metamorphism and this, combined with the probability that they have never been in contact with any other than basaltic material, may explain their ordinariness.

The second factor—the thickness of material traversed—clearly will affect degree of contamination, and in some cases may be important. The Bleiberg ores, investigated by Houtermans and others (1) may well be a case in point here; although the present writers do not know the exact mode of occurrence of the samples measured by Houtermans and his co-workers it is likely that they were taken from "flats" and gash veins closely associated with the bedded lead-zinc ores (of the Silesian type) of the Alpine Triass. These veins are close to the extensive bedded sulfide disseminations, and are very likely derived from these by local ground water activity. In moving from source to host fissure it seems that a relatively small distance has been traversed, hence little or no extraneous lead has been acquired and the vein material is ordinary (in our sense) and uniform. (In fairness it must however be pointed out that the age inferred from the isotope ratios, c.200 m.y., seems very old for such a mechanism.) Had these leads migrated further up the sequence they may well have become anomalous, and lost their uniformity.

The third factor—that of time spent in transit—is tied to the first in so far as the physical nature of the rock is concerned, and is probably of local significance. The rate of migration of lead-bearing solutions will, as is common knowledge, depend on the permeability of the units traversed. Should solutions travel through highly localized and permeable faults or shear zones, they will come in contact with only a relatively small surface area of contaminant and will move past this quickly. If, on the other hand, solutions slowly diffuse through such as a mass of moderately permeable sandstone or limestone, with few or no clearly defined breaks, a far greater surface area is encountered and the two phases are in contact for a greater length of time, leading to heavier contamination.

Thus it must be expected that epigenetic leads will be variably anomalous —indeed it has already been said (p. 591) that ordinary and anomalous leads may simply constitute a series—depending on their histories of migration through the heterogeneous materials of the continental crust. Clearly a great number of variables may contribute to the development of an anomalous lead, and its full derivation may be highly complex. Generally, however, epigenetic galenas occur in folded, metamorphosed and intruded sedimentary terrains, the near-ordinary occurrences are special cases and should be predictable on a fairly simple geological basis. All vein leads, whatever their occurrence, are potentially anomalous and must be highly suspect for dating purposes. Replacement bodies are most commonly in sedimentary environments too, and in such cases they may be distinguishable from morphologically similar syngenetic deposits from lead isotope studies.

In contrast anomalies and irregularities in the relevent syngenetic leads are likely to be rare and only slight when they can be detected. Conformable deposits formed as described might be very slightly contaminated by occluded sea water, and injections of the Sudbury type would undoubtedly incorporate a little foreign material during emplacement. In both cases, however, impurities would bulk so small compared with the material from the main source that deviations would be generally insignificant. Care should be taken here, incidently, not to confuse with conformable concentrations of deep volcanic derivation the small disseminations of galena produced from sea water lead during normal sedimentation.

In spite of these—expectable—variations, a general relationship between lead type and mode of occurrence does seem to be emerging and this should have fundamental implications both in sulfide genesis and in age determination.

CONCLUSION

From the work done so far it appears that the proportions of the different lead isotopes in a given galena may give important information concerning its history.

Variations in the isotope ratios lead to the recognition of lead of two types—ordinary leads and anomalous leads, and different galenas are characterized by one or the other of these. True ordinary leads are probably derived from below the crust, and anomalous leads are derived in turn from these by variable radiogenic contamination in the crust. Thus ordinary and anomalous leads form a series rather than two distinct groups. It is likely, furthermore, that no absolutely ordinary leads occur on the earth's surface, as all have probably received at least minute radiogenic contamination in coming from the mantle.

If the leads of a galena-bearing deposit are anomalous and irregular, they must have migrated some distance through crustal rocks to their present position. Such deposits, whether fracture fillings or constituents of the enclosing rock (replacements) are therefore epigenetic. If leads of a deposit are ordinary and regular, on the other hand, they may be syngenetic. By these criteria it should be possible to determine whether sulfides forming part of a sedimentary rock are syngenetic or epigenetic.

True orthomagmatic leads in mafic rocks should also be essentially ordinary and regular, and should be distinguishable from replacement material in the same way.

All the available lead isotope analyses from conformable deposits fit a single growth curve and hence a single uranium-thorium-lead system. All analyses for individual deposits are also regular, and the lead is therefore probably uncontaminated material of subcrustal origin—in accordance with the theory of genesis enunciated earlier. If all such orebodies have the derivation suggested, it should be possible to date them—and the enclosing rocks—with excellent precision. Clearly it would be interesting at this point to consider the leads of occurrences such as Mansfield, and other conformable deposits of Europe, Africa, and elsewhere.

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SELENIUM IN SOME CANADIAN SULFIDES

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ABSTRACT

Determinations of selenium contents have been made by X-ray spectrographic means on pyrite, pyrrhotite, pentlandite and chalcopyrite from a variety of Canadian ores including a high-intensity magnetite replacement body, several nickeliferous copper sulfide (magmatic) ores of Sudbury, nine massive, non-nickeliferous, copper, iron (zinc) hydrothermal replacement ores chiefly from Quebec and Ontario, ten pyritic gold-quartz deposits, banded siderite-pyrite (chert) deposits, Michipicoten, and pyritic, uraniferous ores of Algoma, Ontario.

Richest selenium concentrations are found in some of the Precambrian non-nickeliferous copper ores, containing several hundred to 1,000 ppm Se, but even in these, relatively selenium-rich and selenium-poor provinces are evident. One Precambrian and two Palaeozoic copper ores are of the latter type. The Sudbury deposits are intermediate between the two extremes, selenium in these averaging between 50 and 100 ppm in the four common sulfides. Pyrites in gold-quartz ores, in the banded Michipicoten deposits and in the uranium ores of Algoma average less than 50 ppm Se but range to below the limit of detectability (15 ppm).

In general no order of preference is indicated by the individual sulfides but in several copper ores and also in the Sudbury ores the tendency is noted for the progressive concentration of selenium with the order of crystallization and in some, amounts in pyrrhotite and chalcopyrite are fairly similar. It is suggested that the apparent lack of order in other deposits may be due to contamination of earlier sulfides in a restricted system by late vapors or copper-rich fluids penetrating earlier minerals.

Variations in selenium with apparent temperature of formation of pyrite in a gold ore, and vertical and horizontal variations in pyrite and pyrrhotite in several of the different types of deposits are noted in addition to distance from intrusives of diabase and quartz porphyry. Selenium is somewhat enriched in lower temperature pyrite, a distinct enrichment is noted in the upper levels of more deeply explored deposits, McIntyre and Noranda, and variations in others occur over shorter distances. Horizontal variations with respect to intrusives are irregular to negligible in some cases, but are more regular in others, selenium being highest at about 100 feet from quartz porphyries (McIntyre) and near the contact of larger diabase dikes (Noranda and Geco). Very extensive sampling of all deposits is required before a clear picture can be obtained of the distribution of selenium in a single ore deposit.

The low to negligible selenium content of gold quartz deposits is attributed to selenium-poor magmatic sources and/or wall rocks. In marked contrast to the selenium-rich uranium ores of the Colorado plateau are the low-selenium siderite ores of Michipicoten, also associated with tuffs, and the (non-tuffaceous) Algoma uranium ores in conglomerates, for the pyrite of which a hydrothermal rather than purely sedimentary origin is favored.

INTRODUCTION

ALTHOUGH selenium has been produced in Canada since 1931 and the annual production has amounted to somewhat over 500,000 lbs. (in 1946 and 1947)

little has been published as to its exact mode of occurrence and distribution in various types of Canadian sulfide-bearing ore deposits.

Production has come entirely from the refining of nickeliferous and non-nickeliferous copper sulfide ores of the Sudbury, Noranda, and Flin Flon areas in Ontario, Quebec and Manitoba-Saskatchewan, respectively. At Noranda, Price (16) has recorded a doubtful occurrence of the copper selenide, klockmannite, CuSe, but it is clear that most if not all the selenium in such ores is present in solid solution in the common sulfides, pyrite, pyrrhotite and chalcopyrite as well as in pentlandite of the nickel ores, in each of which it is able to substitute for sulfur.

An investigation of the selenium content of the common sulfides of some Canadian ores was first undertaken as part of two current studies, one on the trace element content of more or less contemporaneous sulfides in base metal and gold ores with the junior author, the other, on the detailed mineralogy of the ores of Sudbury, Ontario, with Dr. R. L. Stanton. Later this study was expanded to include sulfides in several other types of deposits including a replacement magnetite body, pyrite-siderite ores of Michipicoten, other gold ores and the fairly abundant pyrite and rare pyrrhotite associated with the uranium deposits in conglomerates and other sediments and diabase in the district of Algoma, Ontario, being investigated by P. J. Pienaar. In addition to supplying factual data as to the distribution of selenium in such ores, we have had in mind, the bearing these might have on the origin of many of the deposits.

Previous Work.—Accounts of previous investigations on the selenium content of sulfides are contained in papers by Edwards and Carlos (7) and by Coleman and Delevaux (5) and need not be repeated in detail here.

The mechanism of the substitution of selenium for sulfur in sulfides is well established by the latter two authors who have also reviewed the behavior of selenium under oxidizing and reducing conditions and varying pH.

The possible use of selenium content in distinguishing between pyrite of sedimentary and hydrothermal origin was first indicated in the early studies of Goldschmidt and co-workers, (8, 9) and Carstens (4), analyses showing sedimentary pyrite to be relatively selenium-poor and hydrothermal pyrite somewhat richer.

Edwards and Carlos, in their study of Australian sedimentary, supergene and hydrothermal pyrite, (marcasite), pyrrhotite, chalcopyrite and other sulfides confirmed the low selenium content of sedimentary and supergene samples, but found that hydrothermal sulfides vary in selenium from place to place and suggest that "hydrothermal solutions, as well as meteoric waters, may be deficient in selenium." No distinction is drawn by them as to whether the selenium content of such hydrothermal solutions is related on the one hand to an original magmatic source (though this may perhaps be inferred) or to acquisitions such solutions may obtain or fail to obtain in their passage through various other rocks. In any case, they conclude that "a pronounced selenium content in a sulphide mineral is proof of its hydrothermal or magmatic origin, but absence of selenium is not such positive proof of sedimentary origin."

That there are selenium-rich provinces as indicated by the early work of Williams and Byers (23) is exceptionally well demonstrated by the description by Coleman and Delevaux (5) of selenium occurrences in the uranium-bearing sediments with associated tuffs and in hydrothermal and magmatic deposits in the Colorado plateau region for which the suggestion is made that the "ultimate source of the selenium" in the various sedimentary-volcanic deposits of the area (Colorado Plateau and Wyoming) "can be related to a magmatic province that has contained exceptionally high selenium during periods of volcanic and intrusive activity in Mesozoic and Tertiary times."

These authors recognize that in addition to primary magmatic sources for selenium, hydrothermal solutions may have acquired selenium from the rocks through which they passed, and that selenium in sulfides in certain formations may have been acquired during sedimentary (diagenetic) processes from associated selenium-bearing volcanic debris or even contemporaneous volcanic emanations. In addition, concentration of selenium in sulfides in sediments may be effected by ground-waters near the top of the ground water table. It is clear therefore that care must be taken in drawing inferences as to the origin of sulfides from their selenium content alone, but it is interesting to note the association of high selenium content of all types of sulfides with an ultimate magmatic source.

The actual range and distribution of selenium contents in sulfides in various deposits is of interest in the present study. Carstens (4) found that sedimentary pyrite deposits in Norway contained less than 1 ppm selenium, whereas hydrothermal pyrite contained 20–30 ppm. Goldschmidt and Strock (9) found 9 ppm Se in oolitic pyrite beds, Meggen, Germany, and 7 ppm in oolitic pyrite of strata at Wabana, Newfoundland. Bergenfelt (2) found that pyrite in ores from the Boliden mine, Sweden contained 0.004–0.03 percent Se and chalcopyrite up to 0.14 percent. The order of preferential concentration of selenium in various sulfides was found to be lead-bismuth-antimony sulfides, galena, chalcopyrite, arsenopyrite, sphalerite, pyrite and pyrrhotite.

Edwards and Carlos (7) record that Australian sedimentary pyrite and marcasite have a range from less than 1 ppm to 9 ppm Se, while hydrothermal pyrites show 2 to 132 ppm Se, the majority containing 30 to 50 ppm Se. Pyrrhotites in the same ores contain less than pyrite and range from 1 to 30 ppm Se, chalcopyrites are as rich as, or richer in Se than associated pyrite but amounts are rarely over 100 ppm Se. They find the order of concentration (in decreasing order) in Australian ores examined to be chalcopyrite, arsenopyrite, pyrite, pyrrhotite, sphalerite and galena.

In the sedimentary rocks of the Colorado Plateau region Coleman and Delevaux find the distribution of selenium related to the stratigraphy rather than type of deposit. Maximum amounts of selenium, in part due to the presence of lead or iron selenides, are galena clausthalite, 18 percent, pyrite 5 percent, chalcocite, 5 percent, and marcasite 0.65 percent. In the Triassic Chinle formation, with the exception of the Temple Mountain Deposit, Utah, pyrite and marcasite average .0015 per cent Se as against an average for 8

pyrite samples in Temple Mountain ore of 12 percent and in 4 samples from barren rock of .004 percent. In Cretaceous sediments pyrite or marcasite average .0058 percent, and Tertiary strata (Wyoming) contain pyrite averaging 0.04 percent, and in zones of enrichment, up to 1.5 percent selenium.

Sulfides (copper and iron) associated with clearly defined hydrothermal deposits and laccolithic intrusives of the Colorado Plateau average 0.008 percent, while chalcopyrite from a diorite porphyry shows the greatest concentration of 0.016 percent. Of interest too, in this connection are descriptions of Beath and others (1), cited by Coleman and Delevaux, of selenium-bearing tuffs in the Wind River Basin, Wyoming, containing a maximum of 0.0187 percent Se.

The above data are useful for comparative purposes as some of our Canadian occurrences are considerably richer than those of Australia but are well below some of the sedimentary deposits of the western United States. The decided lack of consistency in the order of concentration of selenium in associated sulfides is also noteworthy and will be considered in connection with the same behavior in Canadian ores.

ANALYTICAL METHOD

In this study selenium analyses have been made entirely by X-ray spectrographic means, using a molybdenum target and a lithium fluoride crystal, with a Philips spectrometer. Operating conditions are as follows:

X-ray tube	—50 Kv, 35 ma
Selenium wave length	—K_α $\lambda = 1.105$, $2\theta = 31.84$[1]
Scaler	—fixed count
Scale factor	—256
Geiger tube	—1,635 volts

Although not sensitive below about 15 ppm Se due to background, the method appears reasonably accurate and has the advantage of ease, rapidity and non-destruction of samples.

Initially, trial working curves were established for the range 30–1,000 ppm Se by plotting percentage selenium against counts per second, using standards in which elemental selenium was mixed with concentrates of each of pyrite, pyrrhotite and chalcopyrite. The pyrite and chalcopyrite were obtained through Dr. R. L. Stanton from Captains Flat, (Lake George Mines) [2] N. S. W., Australia, neither of which gave any X-ray indication of selenium. The pyrrhotite, containing about 30 ppm Se, was from a Sudbury ore. Working curves for each of the three sets of standards were essentially coincident.

Chemical check analyses on four samples analyzed on these preliminary curves were made through the kindness of Michael Fleischer and W. G. Schlecht by chemists of the U. S. Geological Survey. The degree of agreement is shown below.

[1] A check was made for interference by gold, $L\beta_3 - 2\theta = 31.19$ and $L\beta_4$, $2\theta = 31.87$, but none was apparent.

[2] Edwards and Carlos report pyrite from this locality contains 35–36 ppm Se, and chalcopyrite, 29 ppm Se, but as both their and our own experience indicates sulfides in any one deposit may vary considerably in Se content, no allowance was made for Se in these minerals.

CHECK ANALYSES OF SELENIUM IN SULFIDES

No.	Mineral	Location	Preliminary X-ray Se, ppm	U.S.G.S. chemical Se, ppm
N00	Pyrite	Noranda	210	210
N125	Pyrite	Noranda	1,000	1,000
N161	Chalcopyrite	Geco, Manitouwadge	560	600
N174	Pyrrhotite	Geco, Manitouwadge	140	150

Later separate working curves (Fig. 1, 2) were established for pyrite and chalcopyrite, the latter of which appears nearly coincident with the pyrrhotite (N174) analysis of 150 ppm. These curves differ slightly from the preliminary curve, but only in the lower ranges, the two curves converging at

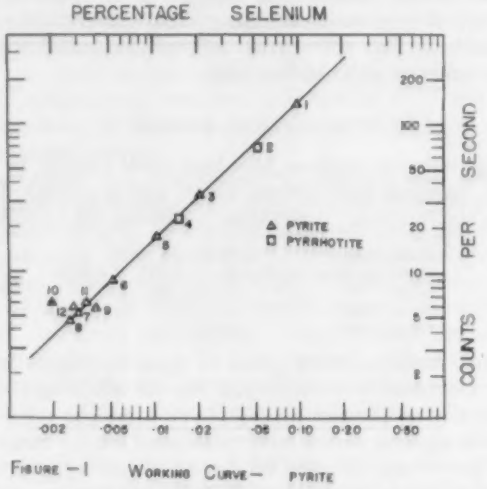

FIG. 1. Working curve for pyrite.

Samples used for Pyrite Working Curve (Fig. 1)

1. Pyrite N125—0.1% Se confirmed by U.S.G.S.
2. Pyrrhotite with 30 ppm Se plus 500 ppm elemental selenium.
3. Pyrite N-00—.021% Se, confirmed by U.S.G.S.
4. Pyrrhotite (Geco) N-174—.015% Se (U.S.G.S.).
5. Pyrite—N-00 diluted with Captains Flat Pyrite—.0105% Se.
6. Pyrite—N-00 diluted with Captains Flat Pyrite—.0052% Se.
7. Pyrite—N-00 diluted with Captains Flat Pyrite—.003% Se.
8. Pyrite—N-00 diluted with Captains Flat Pyrite—.0026% Se.
9. Pyrite—Can. Cop. Ref. (No. 2)—.004(?)% Se.
10. Pyrite—Can. Cop. Ref. (No. 1)—.002% Se.
11. Pyrite—Can. Cop. Ref. (No. 1)—determined by addition method—.0033% Se.
12. Pyrite—Can. Cop. Ref. (No. 2)—determined by addition method—.0029% Se.

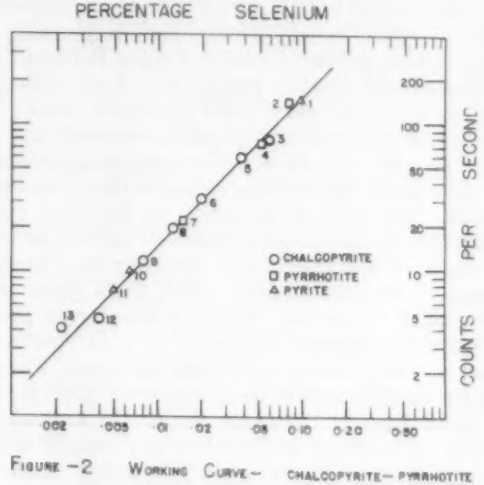

FIG. 2. Working curve for chalcopyrite and pyrrhotite.

Samples used for Chalcopyrite-Pyrrhotite Working Curve (Fig. 2)

1. Pyrite N125—0.1% Se.
2. Pyrrhotite with 30 ppm Se and 800 ppm elemental selenium—.083% Se.
3. Chalcopyrite N161—U.S.G.S.—.06% Se.
4. Pyrrhotite with 30 ppm Se and 500 ppm elemental selenium.
5. Chalcopyrite—Can. Cop. Ref. No. 6—0.039% Se.
6. Chalcopyrite—Can. Cop. Ref. No. 4—0.02% Se.
7. Pyrrhotite—N174 (Geco)—0.015% Se confirmed by U.S.G.S.
8. Chalcopyrite—Can. Cop. Ref. No. 3—0.013% Se.
9. Chalcopyrite—Can. Cop. Ref. No. 2—0.008% Se.
10. Check standard—Captain's Flat chalcopyrite with elemental selenium—66 ppm.
11. Check standard—Can. Cop. Ref. No. 4 diluted with Captain's Flat chalcopyrite to 50 ppm Se.
12. Chalcopyrite—Can. Cop. Ref. No. 1—0.004% Se.
13. Chalcopyrite—Captain's Flat with elemental selenium—22 ppm.

0.1 percent Se. The pyrite curve, Figure 1, was determined on standards prepared chiefly by diluting sample N-00 (above) to several lower concentrations with pyrite from Captains Flat, Australia. In addition, several analyzed samples of the three minerals, obtained through the kindness of Dr. W. C. Cooper, Canadian Copper Refiners, Limited, Montreal, were used in re-establishing the curves.

As a check on the accuracy of the lower extremity of the pyrite curve, two of these samples analyzing chemically, 0.002 and 0.004 percent Se were found by the X-ray method to have .0035 and .0033 percent, respectively. The same samples analyzed by X-ray, by the addition method, in which successive additions of elemental selenium were made and the unknown original

quantity determined, yielded 0.0033 and 0.0029 percent, respectively, differing from the first X-ray results by only 2 and 4 ppm, respectively.

Six chalcopyrite samples from Canadian Copper Refiners Limited, ranged in composition from 0.004 to 0.039 percent Se. Four of these gave an excellent straight line curve, on which N174 pyrrhotite (Geco) with 150 ppm Se (chem.) falls, and the projection of which intersects the plot for N125 pyrite with 1,000 ppm Se. Of the two other samples of chalcopyrite, one fell below and the other above the working curve, so there is no systematic bias. Two other samples were made up as checks on the lower extremity of this curve, one by dilution of a chalcopyrite from 0.02 percent Se to 0.005 percent by addition of Captain's Flat chalcopyrite, the other by a straight addition of selenium to Captain's Flat chalcopyrite. Both check points fall close to the curve and within about 3 ppm Se. To check selenium in pyrrhotites in the higher ranges elemental selenium was added to a pyrrhotite with about 30 ppm Se to bring its concentration to 530 and 830 ppm. Plots of counts per second on these fall on either side of the chalcopyrite curve, the higher concentration almost coinciding with the pyrite curve. As such additions in other cases give a steeper slope to the analytical curve compared with natural minerals, the chalcopyrite curve has been used in reading results on pyrrhotite samples.

The accuracy of the X-ray results thus appears to be of a reasonable order.

SELENIUM CONTENT OF SOME CANADIAN PYRITE

Table 1 presents the analytical results on 173 samples of pyrite from a variety of deposits ranging from a magnetite replacement body, nickeliferous (magmatic) sulfides, massive, non-nickeliferous, copper-iron sulfides with or without zinc sulfide, to pyritic gold quartz ores, banded siderite-pyrite ores of Michipicoten, and the uraniferous pyritic ores and associated rocks of the Blind River district of Algoma, Ontario.

The results clearly show that in these the greatest concentrations of selenium in pyrite are in certain massive copper sulfide deposits such as the Noranda (Horne Mine) Quebec, (Price, 16, 17) and the Geco deposit at Manitouwadge, Ontario (Pye, 15). Of these two deposits the variation in the Noranda samples is much too great (33 to 1,000 ppm Se) to allow any significance to be attached to an overall average of only 32 samples from this large deposit, and although some averages are given in the case of other deposits it is not implied that these necessarily represent true averages for the deposits. Pyrite in other copper deposits of the same general type is somewhat poorer in selenium, and within such ores pyrite with a very low selenium content is present, as well as some with a higher content, e.g., Normetal and Flin Flon.

The selenium in the few available pyrites from the Sudbury ores which are dominantly pyrrhotite-rich, is of the same order of magnitude as in pyrite from some of the less Se-rich massive copper deposits. One sample showing 130 ppm Se from the nickel ores, consists of a spear-shaped aggregate (3″ × ½″) of pyrite penetrating massive nickeliferous pyrrhotite. This may

TABLE 1

SELENIUM IN SOME CANADIAN PYRITES

Type of deposit	Location	No. of samples	Range of selenium content, ppm	Mean selenium content, ppm
Magnetite (Replacement)	Marmora, Ontario	1		<15
Nickeliferous Copper sulfide ores	Sudbury, Ontario	4	25–60	50
		1	130	130
Massive Cu-Fe-(Zn)-S replacement deposits	Noranda, Quebec			
	Upper Levels	6	390–1000	590
	Lower Levels	20	38–445	175
	Lower Levels (run of mine)	6	33–88	63
	Quemont, Quebec	4	40–250	120
	Normetal, Quebec	7	<15	<15
		4	<15–320	155
	Aldermac, Quebec	1		56
	Campbell-Chibougamau, Quebec	1		51
	Geco Mine, Manitouwadge, Ontario			
	250′ Level	14	44–88	60
	50′–450′ Levels	7	50–270	127
	350′ Level	5	97–310	163
	Average	26	44–310	97
	Flin Flon, Manitoba	2		<15
		1		220
Cu-Fe-Zn-S banded ores	Suffield, Quebec	1		<15
	Heath Steele, N. B.	1		20
Gold-pyrite quartz vein	McIntyre Mine, Porcupine, Ontario	21	<15–110	33
	Miscell.—Renabi, Hardrock, Howey-Hasaga (Red Lake) Cathroy-Larder, Ontario; Granada, Quebec; Cariboo, B. C.	10	<15	<15
	Powell Rouyn, Quebec	1		34
	Fondulac, Algold, Sask.	2	23–24	23
Banded Siderite-Pyrite	Michipicoten, Ontario (Rand No. 2)	1		<15
Pyritiferous uranium banded or bedded deposits	*Algoma, Ontario*			
	U-ore in conglom.	26	16–46	28
	Sub-ore conglom. above	2	<15	<15
	and below ore	11	17–39	26
	Polymictic conglom. greywacke matrix, greywacke, calc. greywacke (above ore)	6	17–63	42
	Quasi-basal conglom. (below ore)	2	<15–17	<15
	Argillite (above ore)	1		79
	In Diabase	2	41–43	42
	Pre-Huronian metavolcanics	2	36–47	41

originally have been marcasite, but appears as a hypogene type of replacement in contrast to some supergene marcasite in this area, two samples of which have less than 15 ppm Se.

In general it appears also that pyrite from the more zinc-rich copper sulfide (Palaeozoic) ores such as at Suffield, Quebec (3) and the Heath

TABLE 2

SELENIUM IN SOME CANADIAN PYRRHOTITES

Type of deposit	Location	No. of samples	Range selenium content, ppm	Mean selenium content, ppm
Nickeliferous copper sulfide ores	Sudbury, Ont.			
	North Range	50	18–83	54
	South Range	51	17–230	72
	Total	101	17–230	63
	Alexo, Porcupine, Ont.	1	17	17
Massive Cu-Fe-(Zn)-S replacement deposits	Noranda, Quebec			
	Upper Levels	9	90–555	375
	Lower Levels (23)	8	36–145	97
	Quemont, Quebec	3	54–425	203
	Normetal, Quebec	5	15–235	124
	Aldermac, Quebec	1	74	74
	Campbell-Chibougamau, Quebec	3	<15	<15
		19	20–82	42
	Geco, Manitouwadge, Ontario	10	<15–595	160
	Flin Flon, Manitoba	1		375
Massive Cu-Fe-(Zn)-S replacement deposits, banded	Heath Steele, N. B.	1	21	21
Gold-pyrite-quartz veins	Hollinger, Ontario	1		30
	Discovery-Yellowknife, N. W. T.	1		26
Banded siderite-pyrite	Michipicoten, Ontario (Rand No. 2)	1	<15	<15
Diabase dikes	Algoma uranium district, Ontario. Can-Met mine	1	<15	<15

Steele deposit in New Brunswick, (12) are on the whole very low in selenium, as is some pyrite present with replacement ores of magnetite at Marmora, Ontario.

Pyrite in 34 samples from ten deposits of pyritic-gold-quartz ores (normally considered as hydrothermal) in contrast to the copper ores is also low in selenium, ranging from less than 15 ppm to 110 ppm but averaging less

than 50 ppm, thus agreeing fairly well with hydrothermal pyrites from Australia.

Similarly pyrite, associated with siderite in the widespread Michipicoten iron ores which were considered by Collins et al. (6) as hot-spring replacements, but which have certain sedimentary features and great lateral extent, (18) has a selenium content below our limit of detectability (15 ppm).

Some 50 pyrites[3] associated with the uraniferous conglomerate deposits of the Blind River area, Algoma District, Ontario (13, 10) and with radioactive conglomerates of sub-ore grade, as well as in non-radioactive conglomerates, argillite, pre-Huronian volcanics, and even intrusive diabase bodies, have a selenium content seldom over 50 ppm, grading down to below the limit of detectability. In these rocks pyrite with the highest selenium content (79 ppm) occurs in argillites (above the ore) and in nonradioactive polymictic conglomerates with either a graywacke or argillaceous matrix (42 ppm). Peculiarly two samples from a post-Huronian diabase dike and pre-Huronian volcanics contain the same amount of selenium but about half that in pyrite from argillite.

SELENIUM CONTENT OF PYRRHOTITES

Some 165 selenium analyses of pyrrhotites from five types of deposits are presented in Table 2. Selenium contents range from less than 15 ppm to nearly 600 ppm Se.

In the nickeliferous Sudbury ores about equal numbers of pyrrhotite concentrates from the north and south range deposits show that those from the south average 70 ppm compared with 54 ppm from the north range, with an overall average of over 60 ppm. Although the difference is small it may be of some significance, particularly if the ores arose from some source closer to the south range deposits. In contrast, one sample of pyrrhotite from the small Alexo deposit in the Porcupine district (22) has about the same selenium content (17 ppm) as the lowest in the Sudbury deposits.

Again, as with pyrite, the selenium content of the pyrrhotite from massive copper sulfide replacement bodies is greatest, with the maximum of nearly 600 ppm occurring in pyrrhotite from the Geco mine and almost the same from the upper levels of the Horne mine at Noranda. Some samples of the very similar deposits at Quemont and Normetal are similarly selenium-rich, but others as at Chibougamau (14) and New Brunswick are relatively poorer.

Relatively rare pyrrhotite from pyritic gold deposits, as in the Porcupine district, Ontario, and from one deposit of the Northwest Territories, contains low selenium, 30 and 26 ppm, and slightly less than the average of pyrite in similar deposits.

Rare pyrrhotite in one of the banded siderite-pyrite deposits of Michipicoten, and pyrrhotite in a diabase dike of Algoma both contain less than 15 ppm Se, i.e., below our limit of detectability.

[3] P. J. Pienaar, personal communication, indicates pyrite in these rocks is of two types, one due to sulphidization of black sands, in which pyrite is full of inclusions of iron oxides and associated with zircon, the other euhedral, and free of inclusions. No significant difference in selenium content was found in the two types.

SELENIUM IN PENTLANDITE OF NICKEL ORES

Only preliminary estimates of the selenium content of pentlandite associated with pyrrhotite and chalcopyrite of the Sudbury ores can be given at this time as no check chemical analyses for this mineral are available. Quantities determined have been arrived at by reading counts per second obtained from pentlandite samples, as percentage selenium on the pyrite working curve (Fig. 1). The near coincidence of working curves for pyrite, pyrrhotite and chalcopyrite suggests a similar behavior for pentlandite.

Some 25 pentlandite concentrates were prepared by Dr. R. L. Stanton in connection with another study on the mineralogy of the Sudbury ores and analyzed along with other minerals, details of which will be given in another paper.

Selenium found in pentlandite ranges from 30 to 160 ppm, averaging 85 ppm. Six samples from one orebody on the south range average 97 ppm, five from another average 93 ppm, and four unlocated samples average 45 ppm, while four from one mine on the north range also average 45 ppm Se. The overall average of 17 samples from the south range is 90 ppm Se as against 45 ppm for north range pentlandite, an even greater difference than noted above for pyrrhotites.

Comparing the selenium in pyrrhotites and pentlandites from the same mine or same range, no consistent difference is apparent as might be expected from their common ex-solution relations. In two deposits there is somewhat more selenium in pentlandite than in pyrrhotite, but in two others the reverse is true.

SELENIUM IN CHALCOPYRITES

The selenium contents of 66 samples of chalcopyrite from various types of deposits are shown in Table 3. The range is from 33 to 540 ppm Se.

As is the case with pyrite and pyrrhotite, chalcopyrite in the non-nickeliferous, massive, copper sulfide ores is in some cases richest in selenium while others of the same class either approach chalcopyrites of the nickeliferous ores or average even less.

Only one chalcopyrite from a gold ore was available for analysis and appears to contain slightly less selenium than either the pyrite or pyrrhotite of similar deposits.

DISTRIBUTION OF SELENIUM IN DIFFERENT SULFIDES OF CANADIAN ORES

As shown in the review of previous work there is no regular order of concentration of selenium in the common sulfides of different ores. This is amply born out by Canadian occurrences that show wide variations in selenium content in single sulfides in individual deposits, a variable order and degree of concentration in different deposits, but a rather similar enrichment of selenium in all three or four sulfides (pyrite, pentlandite, pyrrhotite and chalcopyrite) in the somewhat selenium-rich areas, and a similar deficiency in the associated sulfides of selenium-poor ores.

Although the sampling from many of the deposits is probably far from adequate, we may note that for nine deposits the maximum concentrations of selenium so far determined are in pyrite of three deposits, Noranda (1,000 ppm), Normetal (320), McIntyre, Hollinger (33); in pyrrhotite of three deposits or areas, Geco (595), Quemont (425), Sudbury (230); and in chalcopyrite of three, Flin Flon (470), Aldermac (135), and Chibougamau (94 ppm Se). In the latter three and also in Noranda, Normetal and Geco, selenium maxima in both pyrrhotite and chalcopyrite are much the same in the two minerals, reflecting in these cases, perhaps, the usual close relation

TABLE 3

SELENIUM IN SOME CANADIAN CHALCOPYRITES

Type of deposit	Location	No. of samples	Range selenium content, ppm	Mean selenium content, ppm
Nickeliferous copper sulfide ores	Sudbury, Ontario			
	North Range	1		34
	South Range	21	33–165	100
	Average of all	22	33–165	97
Massive Cu-Fe-(Zn)-S replacement deposits	Noranda, Quebec Upper Levels	7	360–535	430
	Quemont, Quebec	3	40–280	147
	Waite Amulet, Quebec	1		395
	Normetal, Quebec	8	23–260	114
	Aldermac, Quebec	1		135
	Campbell-Chibougamau, Quebec	9	25–94	58
	Geco, Manitouwadge, Ontario	10	130–540	260
	Flin Flon, Manitoba	4	145–470	251
Gold-pyrite veins	Hollinger, Ontario	1		23

in time of deposition of the two minerals as compared with pyrite. In only three deposits, Flin Flon, Aldermac, and Chibougamau, is a consistent order of concentration found for the maximum amounts, namely, in decreasing order, chalcopyrite, pyrrhotite and pyrite, the reverse of the paragenetic sequence. This order, however, also holds for the averages of selenium in the Sudbury sulfides which show less wide variation than several of the copper ores. At Sudbury average concentrations of selenium are chalcopyrite (97 ppm), pentlandite (85), pyrrhotite (63) and pyrite (50). It is questionable if the averages of the copper deposits are very meaningful due to the wide variations found, but in five of these the average content in chalcopyrite is greater than in the other two sulfides.

In the selenium-poor mines or areas the two or more associated sulfides are consistently low in selenium.

Where amounts of selenium are at all significant in Canadian deposits, we may note that all three or four associated sulfides studied may have quantities of much the same order, with a general but not consistent tendency for it to be concentrated most in chalcopyrite, not withstanding the occasional high content of pyrite. In some the order is the reverse of the paragenetic sequence, but in others it is not. Although no one sulfide is consistently the best host, there is a tendency for it to be concentrated in the last common sulfide to crystallize.

Before considering this subject further, variations in selenium content of individual sulfides will be considered with respect to temperature of formation of some pyrites, to vertical and horizontal extent of pyrite and pyrrhotite in some deposits, distance from intrusives such as porphyries and diabase dikes and type or locality of deposits.

TABLE 4

SELENIUM CONTENT OF PYRITE AT MCINTYRE

Depth	No. samples	Se ppm in low temp. pyrite	No. samples	Se ppm in high temp. pyrite
1,000′–2,500′	4	60	6	33
2,655′–6,400′	4	22	7	22

VARIATION IN SELENIUM IN PYRITE OF DIFFERENT TEMPERATURE OF FORMATION

An opportunity to study variations in selenium in pyrites was available using samples from the McIntyre mine on which Smith (19) previously determined temperature effects and on which the senior author (11) reported variations in trace elements.

As noted above pyrites from the McIntyre gold mine contain only moderate to low amounts of selenium, 21 samples averaging 33 ppm Se, with a range from less than 15 ppm to 110 ppm. Of these, eight samples of "low temperature" pyrite showing heat effects at temperatures of 125–175° C, contain an average of 41 ppm Se, whereas 13 of "high temperature" pyrite (430–575° C) contain on the average only 27 ppm Se.

Although this difference is rather distinct, as shown below it may be due in part to factors other than temperature of formation.

VARIATION IN SELENIUM IN SULFIDES WITH DEPTH

Samples of sulfides from four different deposits allow comparison of their selenium content at different levels in the mines. These are the McIntyre gold deposit, and the copper deposits at Noranda, Chibougamau, and Manitouwadge.

As shown by Table 4, the higher selenium content of both the low- and

high-temperature pyrite appears related to depth, and although the former contains about twice the selenium of the latter in the upper levels, at greater depth, both have the same amount.

The most pronounced vertical variation found is in the Noranda deposits as summarized in Table 5. Samples from the upper levels were collected many years ago from the 100 and 200-foot levels of orebodies A, B, D and E. Samples from the lower levels include some from both the 23A sub-level and the 31st level obtained through the kindness of Dr. Peter Price, particularly to study variations in the sulfides adjacent to the well-known North-South diabase dike. Unfortunately samples from intervening levels have not been available, but the change of selenium concentration with depth would seem to be clearly indicated in both pyrite and pyrrhotite concentrates, the near surface enrichment being very marked.

TABLE 5

SELENIUM CONTENT OF NORANDA PYRITE AND PYRRHOTITE WITH DEPTH
(Se in ppm)

Depth	Pyrite			Pyrrhotite		
	No. of samples	Range	Mean	No.	Range	Mean
Upper levels 0–200'	6	390–1,000	*590*	9	90–555	*375*
23A sub-level	14	38–262	132	7	36–143	100
31st level	6	142–330	275			
Lower levels 23A, 31st (average)	20	38–445	*175*			
Lower levels (run of mine)	6	33–88	*64*			

Between the 23rd A sub-level and the 31st level a rise in selenium content of pyrite is apparent, though it should be noted samples from the 23-A sub-level come from massive ore west of the diabase dike and those on the 31st level are from a smaller tongue of sulfides on the east side of the same dike. The discrepancy between the selenium of six "run-of-mine" samples, recently submitted from this deposit and selected samples from the 23A and 31 Levels is probably indicative of the heterogeneous distribution of selenium in this ore.

In the Campbell-Chibougamau mine, Quebec, samples collected for us by Dr. Gilles Allard, cover a vertical range from the 250 to the 1,150-foot levels. Of the three common sulfides, only pyrrhotite was present in sufficient amounts in all samples to permit a comparison with depth.

Here, as shown in Table 6, only moderate variations occur in the concentration of selenium with depth. At and above the 448-foot level, samples average 40 ppm; on the 550 to 850-foot levels Se decreases to about 22 ppm but on the 1,000 and 1,150-foot levels it increases again, averaging 66 ppm Se.

In the Geco deposit at Manitouwadge, although the vertical range is relatively small, some variation in selenium content in all three sulfides is apparent (Table 7), some samples of the three sulfides from the 250-foot Level con-

taining the most selenium, while lower amounts are present both above and below this level.

From the above it is clear that in the more deeply explored deposits of both copper and gold types, selenium is more concentrated in the upper levels than in the lower. In two deposits explored only to relatively shallow depths,

TABLE 6

SELENIUM IN CAMPBELL CHIBOUGAMAU PYRRHOTITE WITH DEPTH
(Se in ppm)

Depth	No.	Range	Mean Se
250–448′ L.	7	32–47	40
550–850′ L.	9	15–51	22
1,000–1,150′L.	5	49–82	66

variations in selenium occur over a few hundred feet, one decreasing and then increasing at depth, the other increasing first and then decreasing. The reason for such variations is not clear, but it is apparent that careful and extensive sampling will be required for at least some deposits, before a clear picture is available of the over all distribution of selenium in single ore deposits.

TABLE 7

SELENIUM IN GECO SULFIDES
(with depth)
(parts per million Se)

Depth	Pyrite			Pyrrhotite			Chalcopyrite		
	No. of samples	Range	Se	No.	Range	Se	No.	Range	Se
50′ level	(1)	(70)	70	(2)	50–250	150	(2)	135–210	170
250′ level	(3)	(50–270)	190	(4)	21–595	180	(2)	230–540	385
	(14)	(40–80)	60						
350′ level	(5)	(130–310)	160						
450′ level	(1)		100				(1)		170

LATERAL VARIATIONS IN SELENIUM IN SULFIDES OF SINGLE ORE BODIES

Samples from one nickel and two copper orebodies were obtained in order to study the lateral variations of selenium (and other trace elements) in individual sulfides and particularly to determine any relationship to their proximity to crosscutting diabase dikes. In the nickel orebody at Fecunis Lake, north range, Sudbury area, pyrrhotites were available in samples spaced up to 4 feet on either side of a 4-foot diabase dike. From Geco mine, pyritic samples adjacent to the east side of a small 15-foot dike (Dyke A) on the

250-foot Level, and from the west side of a much larger dike on the 250-foot Level, were analyzed. At both Fecunis Lake and Geco no question seems to have been raised as to the post-ore age of the dikes. At Noranda pyrite-rich samples from the 23A sub-level and 31st levels are from the west and east sides, respectively, of the well-known north-south diabase dike, which was considered as post-ore at first, but latterly as pre-ore in age (20).

TABLE 8

SELENIUM, COBALT AND NICKEL IN PYRRHOTITE—FECUNIS LAKE, ONTARIO
(with distance from diabase dyke)

Sample No.	Distance from dike	Selenium, ppm	Cobalt, %	Nickel, %
A-1	0′ E	49	.047	1.60
A-2	6″ E	53	.035	1.40
A-3	1′ E	54	.042	1.45
A-4	1′ 5″ E	48	.033	1.10
A-5	2′ E	61	.037	1.27
A-6	3′ E	68	.032	1.25
A-7	4′ E	53	.037	1.22
	Average	55	.038	1.33
C-1	0′ W	54	.032	1.12
C-2	6″ W	48	.036	1.37
C-3	1′ W	53	.032	1.22
C-4	1′ 5″ W	47	.041	1.35
C-5	2′ W	49	.040	1.50
C-6	3′ W	57	.057	1.25
C-7	4′ W	52	.035	1.40
	Average	51	.039	1.34

Samples of pyrite from the McIntyre mine permit a study of the lateral variation of both low and high temperature pyrite with respect to distance from quartz-porphyry intrusives. The results are given in the following tables 8 to 10, in some of which cobalt and nickel contents are included for comparison.

TABLE 9

SELENIUM IN PYRITE—GECO MINE
(350′ Level—West of "Big" Diabase Dike)

Sample No.	Distance from diabase	Se in pyrite, ppm
11	2′	310
12	8′	133
13	15′	155
14	36′	120
15	43′	97

In the Fecunis Lake nickeliferous pyrrhotite (Table 8) the variation in selenium as well as in cobalt and nickel is remarkably slight on both sides of the small diabase dike cutting the ore.

At the Geco mine a similar constancy in selenium content in pyrite has been found over a lateral distance of 25 feet from the small dike on the 250-

foot level, the amounts ranging irregularly from 44 to 88 ppm Se with no discernible trend. On the 350-foot level however, Table 9, a fairly distinct decrease in selenium in pyrite is noted, away from the larger "Big" diabase dike, width of which is over 100 feet.

Variations in selenium in pyrite of Noranda ores lying on either side of the 80-foot wide, north-south, diabase dike have also been examined (Table 10). On the 23A sub-level samples were spaced from 0 to 140 feet west

TABLE 10

SELENIUM, COBALT AND NICKEL IN PYRITE—NORANDA
(23A sub-level and 31st level)

Sample No.	Distance from diabase	Selenium, ppm	Cobalt, %	Nickel, %
23A sub-level				
23-1	0′ W	160	.0265	.0013
23-2	1′	135	.0265	.0013
23-3	2′	103	.0265	.0010
23-4	5′	118	.0280	.0012
23-5	10′	143	.0275	.0015
23-6	20′	210	.038	.0009
	Average	144	.027	.0012
23-7	30′	140		
23-8	40′	167		
23-9	50′	75		
23-10	65′	38		
23-11	80′	262		
23-12	100′	138		
23-13	120′	45		
23-14	140′	120		
	Average	124		
31st level				
31-1	0′ E	330	.0210	.0015
31-2	1′	300	.0095	.0006
31-3	2′	445	.0200	.0009
31-4	5′	252	.0125	.0008
31-5	10′	177	.1250	.0011
31-6	20′	142	.0105	.0010
	Average	275	.014	.0010

of the dike. Selenium varies irregularly from about 40 to 260 ppm. In the first 20 feet away from the dike six samples average 144 ppm, and in the remaining distance, to 140 feet, 8 samples average 124 ppm, but there is no systematic variation on this level. In comparison cobalt and nickel are in general more constant.

On the 31st level of Noranda, on the other hand, not only is the selenium in the pyrite greater in amount than on the 23rd level, but a considerable decrease is evident from 2 to 20 feet east of the diabase. In both cases the selenium in pyrite at the diabase contact is slightly above the averages given.

Variations of these samples in cobalt and nickel are greater than on the 23rd level, but no relation exists between them and selenium content.

Samples of pyrite from the McIntyre gold ores similarly show some variation laterally as measured by distances from nearby quartz porphyry intrusives. Range of selenium is from less than 15 ppm to 83 ppm for the high-temperature pyrite and to 110 ppm for the low-temperature pyrite. In both cases the greatest quantities are present in pyrite spaced at 105 and 100 feet, respectively, from quartz porphyries, with lesser quantities on either side. This of course may be simply a coincidence, but is noted here, as Smith indicated a distinct temperature gradient about the intrusives to which the mineralization is believed related.

DISTRIBUTION OF SELENIUM WITH TYPE AND LOCALITY OF DEPOSIT

The above data indicates rather clearly that the major concentration of selenium (over 100 ppm) in the Canadian Precambrian deposits studied is in most of the massive copper, iron sulfide replacement types of deposits, considered usually as hydrothermal in origin. One exception, Chibougamau, contains amounts (50–100 ppm) about the same as the (magmatic) nickeliferous copper sulfides of the Sudbury area, but both of these are higher in selenium than the Palaeozoic copper ores ($\backsim$ 20 ppm) of a somewhat similar type in the Eastern Townships, Quebec, and in New Brunswick.

Other selenium-poor ores include a magnetite replacement ore; the hypothermal types of gold ores; the peculiar banded siderite-pyrite-chert ores of Michipicoten attributed to replacement of tuffs by volcanic emanations, but the great lateral extent of which suggests also a sedimentary history; and the pyritic-uranium ores and sub-ore zones in conglomerates and associated sediments of Algoma, Ontario, the origin of which is still unsettled, but may include reworking of some sedimentary material.

DISCUSSION

From the foregoing some observations may be made on the distribution of selenium in the deposits for which a fair number of samples are available.

In the nickeliferous copper sulfide ores of the Sudbury area the distribution of moderate quantities of selenium (50–100 ppm) in pyrite, pyrrhotite, pentlandite and chalcopyrite is considerably more uniform (Table 8) than in the richer non-nickeliferous copper ores. This appears in keeping with a magmatic sulfide origin for the major part of these ore bodies. Furthermore the average selenium contents of the four sulfides indicate a gradual enrichment of selenium with progressive crystallization. The one analysis of a peculiar spear-shaped mass of pyrite, believed of late hypogene replacement origin, containing 130 ppm Se, conforms to this general order of increasing selenium with age of deposition. In contrast, late, supergene marcasite in a few of these ores is very low in selenium. The effect of a narrow post-ore diabase dike at the Fecunis Lake deposit (North Range) on both the selenium and other trace elements (with the exception of silver) in adjacent pyrrhotite is

negligible. The somewhat higher selenium in both pyrrhotite and chalcopyrite from south range deposits compared with north range ores, may conceivably be related to the proximity of the former to the original magmatic source. Compared with similar ore from Tasmania (Edwards and Carlos) containing 42 ppm Se, the Sudbury ores are somewhat richer.

In the relatively selenium-rich copper sulfide ores as in the Noranda area and Manitouwadge, although the average selenium contents of the three common sulfides are not too dissimilar, the ranges in concentration are much greater than in the nickel ores. At Noranda a rather distinct vertical variation has been noted, the sulfides in the upper levels being relatively enriched (Table 5) while at Geco and Chibougamau vertical changes are present though less well-defined. Horizontal variations in pyrite of the massive sulfide replacement body at Noranda (Table 10) are peculiar, particularly if one considers that the pyrite was deposited more or less contemporaneously from a uniform ore fluid. That such was essentially the case is suggested by the rather uniform cobalt and nickel content. How then may the greater differences in selenium be explained? A possible explanation for the Noranda deposits in particular, and perhaps for others showing similar variations, is that the several sulfides, deposited progressively in what was probably a restricted system, as indicated by the paragenesis, may have acquired additional selenium at various times after their original deposition from vapors or later ore fluids during progressive fracturing and possibly some recrystallization. This is supported to some extent by the general tendency noted for selenium to be enriched in the paragenetically late chalcopyrite, and is in keeping with Price's explanation of the irregular distribution of the individual sulfides and gold in the Noranda ore bodies.

In the various copper ores studied, one of the variations in mineralization is the amount of sphalerite present. No relation appears to exist however between this mineral and the selenium content of the associated iron-copper sulfides. Ores fairly rich in selenium at Flin Flon, Normetal, and Geco carry considerable sphalerite in places, as do the selenium-poor ores at Suffield, Quebec, and New Brunswick. In the Geco mine, seven pyrite samples from a zinc-rich zone on the 250-foot level (2–12 slot drive) averaged 61 ppm Se, and seven from zinc-poor ore, 15 feet away, averaged 58 ppm Se.

The lower content of selenium in the Chibougamau copper deposit, and still lower quantities in Palaeozoic ores of Quebec and New Brunswick, may be due either to their derivation from magmas in selenium-poor provinces or to some other factor in their history. The same applies to the hydrothermal gold-pyrite-quartz ores, the very low selenium content of some of which in no way distinguishes them from sedimentary pyrites, although in others selenium is above the sedimentary range.

The results on the McIntyre pyrite samples on which Smith's studies indicated a range in temprature of deposition from over 500° C down to 125° C, show selenium concentrated somewhat more in the lower temperature types, in pyrite from the upper compared with the lower levels, and at a distance of about 100 feet from quartz-porphyry bodies for both types of pyrite. Thus

temperature, pressure, and selenium-content of ore fluids at various times appear as factors determining the selenium content of this sulfide.

The fact that the lower limit of detectability of our analytical method is not sufficient to indicate exactly the content of many of the selenium-poor ores, precludes the drawing of any firm conclusions with respect to them. The apparently low to negligible content of the pyritic gold ores, whether derived from deep magmatic sources and deposited from hydrothermal solutions or, as Sullivan (21) suggests, formed by granitization of chloritized and carbonated lavas, would in any case indicate either selenium-poor magmas, or selenium-poor, earlier volcanics, or both.

The low selenium Michipicoten siderite-pyrite ores, closely associated with Keewatin lavas and pyroclastics, and the Algoma pyritic uraniferous conglomerates (in sediments devoid of tuffs), are in marked contrast to the selenium-rich Colorado plateau uraniferous deposits which have been related to penecontemporaneous volcanic and intrusive activity. Quantities of selenium found in the Algoma deposits however, are above those noted by others as characteristic of purely sedimentary deposits and the manner of occurrence of the pyrite in this locality is more typical of hydrothermal introduction, even if from a selenium-poor source.

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COAL STRATIGRAPHY AND RESOURCES STUDIES, 1949–1957

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ABSTRACT

More than 300 papers dealing with stratigraphy and resources studies on coal-bearing rocks in the United States and Canada have been published during the past 9 years. Most of these have been published by the U. S. Geological Survey, the U. S. Bureau of Mines, and the state surveys for Illinois, Indiana, Kansas, Kentucky, Missouri, Ohio, Pennsylvania, and West Virginia.

The U. S. Geological Survey has published more than 40 Coal Investigations Maps, which cover 7½-minute quadrangles, 15-minute quadrangles, coal fields, or coal districts. Circulars have been published which include the calculation of coal reserves for Colorado, Indiana, Michigan, Montana, New Mexico, Oklahoma, Oregon, North Dakota, South Dakota, Virginia, and Wyoming. The U. S. Bureau of Mines has completed more than 40 county reports which estimate the known recoverable reserves of coking coal in Kentucky, Maryland, Pennsylvania, Tennessee, and West Virginia.

INTRODUCTION

Stratigraphy and coal resources studies include descriptive field work, supplemented by laboratory work, on coals and coal-bearing rocks. An understanding of the stratigraphy is necessary for the calculation of coal reserves. As one works out the stratigraphy in an area he must observe details of structure and sedimentation, and he may make a special study of the distribution, thickness, and relationship of certain lithologic units. In order to calculate reserves accurately he must obtain information on thickness of each coal, thickness of overburden for each coal, altitude of the coal, interval between coals, areas and amount of convergence or splitting of the coal, area and kinds of coal cutouts, and kind of roof and floor and the suitability of each coal for mining. Thus, most of the publications that include coal reserve calculations also include information on stratigraphy and commonly on sedimentation and structure. Certain research on plant spores in coal, coal petrography, and coal chemistry may be closely allied to stratigraphy and resources studies but the above three areas of study are not included in this review.

This report summarizes the literature on the stratigraphy of coals and adjacent rocks and on coal reserve studies in the United States. No attempt is made to analyze or evaluate the numerous projects which are now underway but the results of which have not been published. The literature reviewed is those papers published since the summary of the status of coal resources studies was presented by Searight in 1948 (202) to the Committee on Coal Research, Society of Economic Geologists. Thus it includes papers published in 1949 and the succeeding years. A bibliography of publications of the U. S. Geological Survey that were related to coal and were published between 1882 and 1949 was compiled by Berryhill (28). At this time the Coal Committee of the Society of Economic Geologists began a program of compilating annual bibliographies on coal geology. Bibliographies were done by Cross for 1950 (65), Miller for 1951 (166), and Wier for 1952 (279) but none have been compiled since.

FIELD CONFERENCES

Recent interest in the geology of coal-bearing rocks is indicated by the number of special field conferences that has been held in Illinois, Indiana, Kansas, Kentucky, Missouri, Ohio, Pennsylvania, and West Virginia. Wanless conducted the trip in Illinois in 1955 (267) mostly in Fulton County, west central Illinois. Excellent exposures that ranged in age from the Tarter coal in the lower part of the Tradewater Group to the Herrin (No. 6) coal in the upper part of the Carbondale Group were visited. Two conferences have been held in Indiana on Pennsylvanian rocks. Wier and Esarey in 1951 (284) conducted a field conference that included sections in the upper part of the Pottsville, the Allegheny, and the Conemaugh Series in west central Indiana. A second conference was led by Gray in 1957 (116) in the southern part of the outcrop area and included exposures of Pottsville rocks. Jewett in 1957 (138) was in charge of a conference in eastern Kansas that covered lower Permian and Pennsylvanian rocks. Huddle in 1953 (134) conducted a conference that included rocks in the lower part of the Breathitt Formation of Pennsylvanian age in Morgan, Magoffin and Breathitt Counties in eastern Kentucky. Searight in 1955 (203) led a field trip that studied rocks of Des Moinesian age in western Missouri. Cross in 1950 (69) conducted a field trip in the northern part of the Dunkard Basin in Ohio, Pennsylvania, and West Virginia. Outcrops studied are in the Greene, Washington (Permian), and Monongahela (Pennsylvanian) Series. Coal-bearing rocks were discussed in other field conferences such as those held in Montana (77), New Mexico (32), and Wyoming (30, 135).

COAL RESOURCES

Most of the work done on coal resources during the past 9 years has been done by the U. S. Geological Survey, the U. S. Bureau of Mines, and the various state geological surveys.

The U. S. Bureau of Mines has been accumulating and interpreting information on coal that is suitable or could be made suitable for the manufacture of metallurgical coke. Reports on selected coal fields or districts in Alabama, North Carolina, Colorado, and Maryland have been published. In addition to data on coal reserves, these reports include information on stratigraphy and chemical, petrographic, and coking characteristics of the coals. Also, the Bureau has completed more than 40 county reports that estimate the known (measured and indicated) and recoverable reserves of coking coal in Kentucky, Maryland, Pennsylvania, Tennessee, and West Virginia (Table 1).

The U. S. Geological Survey has emphasized detailed geologic mapping of coals and calculation of coal reserves by states. Nearly 40 geologic maps have been published in the Coal Investigations series during the past 8 years. Most of these have been published in cooperation with state surveys in Colorado, Indiana, Kentucky, Montana, New Mexico, North Carolina, North Dakota, Pennsylvania, South Dakota, Washington, and Wyoming. Some

of these maps cover 7½ minute or 15 minute quadrangles, some cover coal fields or districts, and others cover an entire state. The Survey has published other reports on specific coal fields or districts for areas in Alaska, Idaho,

TABLE 1

KNOWN AND KNOWN RECOVERABLE RESERVES OF COKING COAL ESTIMATED BY COUNTY IN 5 STATES BY THE U. S. BUREAU OF MINES (IN MILLIONS OF SHORT TONS)

State	County	Known reserves	Known recoverable reserves
Kentucky	Floyd (93)	1,670	694
	Harlan (258)	2,138	1,122
	Knott (95)	1,859	624
	Letcher (257)	1,353	571
	Perry (261)	840	403
	Pike (89)	3,916	1,757
	Total	11,776	5,171
Maryland	Allegany (254)	556	152
Pennsylvania	Allegheny (256)	832	384
	Armstrong (90)	1,550	574
	Cambria (87)	2,407	931
	Clarion (33)	1,210	428
	Fayette (92)	943	460
	Greene (263)	6	4
	Indiana (88)	2,544	974
	Jefferson (94)	710	252
	Somerset (255)	1,859	773
	Washington (262)	4,181	2,284
	Westmoreland (91)	992	523
	Total	17,234	7,587
Tennessee	Bledsoe (292)	43	11
	Campbell (293)	398	149
	Claiborne (130)	60	32
	Fentress (157)	102	41
	Grundy (128)	15	6
	Hamilton (131)	53	17
	Marion (290)	61	34
	Morgan (294)	96	30
	Overton (288)	19	6
	Putnam (287)	29	17
	Scott (291)	143	39
	Sequatchie (289)	76	31
	Van Buren (129)	34	8
	Total	1,129	421
West Virginia	Brook (97)	191	104
	Logan (230)	5,411	2,391
	Marion (188)	3,141	1,579
	Marshall (99)	3,158	1,416
	McDowell (252)	2,217	1,075
	Mercer (260)	188	52
	Mingo (259)	3,007	1,365
	Monongalia (240)	3,526	1,577
	Ohio (98)	365	162
	Raleigh (96)	2,532	1,291
	Wyoming (253)	2,665	1,167
	Total	26,401	12,179

Montana, North Dakota, South Dakota, Ohio, and Wyoming. Coal reserves have been computed, and coal reserve information published for Colorado, Indiana, Michigan, Montana, New Mexico, North Dakota, Oklahoma, Oregon, South Dakota, Virginia, and Wyoming. Since 1948, state geological surveys have completed similar coal reserve reports for Illinois, Ohio, and Kansas (Table 2).

Methods of Reserve Calculation.—Since 1928, when the latest estimate of coal reserves in the United States was made by M. R. Campbell of the U. S. Geological Survey, many detailed maps of local coal fields throughout the United States have been completed both by the U. S. Geological Survey and by state geological surveys, and much exploration and development have

TABLE 2

COAL RESERVE STUDIES BY STATES
(IN MILLION OF SHORT TONS)

State	Original reserves	Remaining reserves	Date
Alaska (17, 18, 143, 250)	2,286	—	1-1-49
Colorado (222)	100,408	99,450	1-1-52
Illinois (53)	—	137,329	1-1-50
Indiana (221)	37,293	35,806	1-1-51
Kansas (11, 198, 200)	—	20,774	1-1-50
Michigan (58)	297	220	1-1-50
Montana (59)	222,047	221,779	1-1-49
New Mexico (189)	61,755	61,516	1-1-48
North Dakota (37)	350,910	350,768	1-1-51
Ohio (40)	43,855	40,000	1-1-56
Oklahoma (241)	3,673	3,245	1-1-53
Oregon (163)	200	194	1-1-54
South Dakota (44)	2,033	2,031	1-1-51
Virginia (42)	12,051	11,119	1-1-51
Wyoming (25)	121,554	120,753	1-1-50

been carried on by private companies. The recent resources studies by the U. S. Geological Survey were done in accordance with a recommendation of the National Bituminous Coal Advisory Council in December 1948 to the Secretary of the Interior. The recommendation was prepared by the Coal Resources Committee of the Council and was entitled: A plan for a rapid reappraisal of minable bituminous coal resources of Pennsylvanian age east of Mississippi River on the basis of information now available. The scope of these studies has been expanded to include states west of the Mississippi River, to include coals of Triassic, Cretaceous, and Tertiary age, and to include all ranks of coal. Current summary appraisals of total reserves will be prepared for most of the United States, by classes according to thickness of bed, amount of overburden, reliability of information, and other pertinent factors. The U. S. Geological Survey, with cooperation from state surveys, mining companies, and private individuals, has undertaken this work and expects to continue it until a new appraisal of total reserves in the United States has been completed.

The U. S. Geological Survey and the U. S. Bureau of Mines have agreed

on certain rules for calculating coal reserves which supplement the recommendation of the National Bituminous Coal Advisory Council. Although some variations in categories are used in each report, in general, the following rules and definitions are followed by both Federal and State agencies.

Reserves are calculated for each coal bed in categories of area, thickness, depth or overburden, reliability, and rank. The geographic area may be by township, county, field, or other recognizable area. The thickness categories for each coal that are commonly used are: 14 to 28 inches, 28 to 42 inches, and more thar 42 inches. Some reports on subbituminous coal and lignite use: 2½ to 5 feet, 5 to 10 feet, and more than 10 feet. Depth categories are commonly: less than a foot to 1,000 feet, 1,000 to 2,000 feet, and 2,000 to 3,000 feet. Reserves are not calculated for coals deeper than 3,000 feet. In an area where coal is near the surface and may be mined by stripping, the coal is classified as strippable or nonstrippable on the basis of an arbitrary thickness of overburden such as 60, 90, or 150 feet. Overburden categories are similar to the following: less than a foot to 60 feet, 60 to 90 feet, 90 to 120 feet, and 120 to 150 feet.

The three classes of reliability are measured, indicated, and inferred. These are approximately equivalent to the terms proved, probable, and possible, which have been used by some in coal mining and in other mineral industries. Evaluation of the reliability of reserves is slightly different for each area and each coal and depends mostly on the knowledge of the continuity of the coal or lack of it.

Measured reserves are presumed to be within 20 percent of the true tonnage. The points of observation are, in general, half a mile apart. The outer limit of a block of measured coal, therefore, is a quarter of a mile from the last point of positive information. If drilling or mining information is not available, and if the outcrop is continuous for miles, the measured reserves occur in the strip half a mile wide along the outcrop.

Indicated reserves are less reliable than measured reserves and occur farther away from points of information. In general the points are 1 mile apart. Thus, because measured reserves extend a quarter of a mile from the point, indicated reserves are in the area from a quarter of a mile to half a mile from each point. If no data are available other than the outcrops, and if the continuity of the outcrop is measured in miles, indicated reserves occur in a band between half a mile and 2 miles from the outcrop line.

Inferred reserves are the least reliable and lie outside the limits of measured and indicated reserves. These reserves are based on assumed continuity of the coal in accordance with geologic evidence. If a bed is known to be discontinuous, the geologist probably will not calculate inferred reserves.

Coal reserves also are placed in categories according to rank. This is necessary for accurate calculations because the higher rank coals weigh more per cubic area than the lower rank coals and thus contain more tons per acre per foot of coal. Somewhat arbitrarily the short tons per acre-foot are as follows: anthracite and semianthracite, 2,000; bituminous coal, 1,800; subbituminous coal, 1,770; and lignite, 1,750. Some reserve calculations have

deviated from this. For example, 1,770 tons per acre foot instead of 1,800 has been used for bituminous coal in Illinois.

The above discussion concerns original reserves. To obtain remaining reserves that coal mined and lost to future mining must be subtracted from the original reserves. Recoverable reserves are commonly considered to be 50 percent of the remaining reserves, but the percentage varies according to the type of mining, amount of preparation, and characteristics of the individual coal bed. For example, strip mines may recover 85 percent or more of the total coal in the ground.

Although the categories used in the reserve calculations made in the various states do not conform exactly to any one standard, the results can be integrated if the categories used are carefully explained and defined.

Reserve Summaries.—Information on coal resources in the United States has been summarized by Averitt and Berryhill in 1950 (10), in 1952 (9), and in 1953 (11) and by Ball in 1954 (13). Other summaries of information were prepared in 1951 on coking coal resources of the United States by Toenges (232) and of the western United States by Berryhill and Averitt (29).

In 1952 the Corps of Engineers released a report on the synthetic liquid fuel potential of the United States (61). This report included tables of coal reserves for each state and included only those reserves which are in blocks of more than 30 million tons for underground mining and more than 5 million tons for strip mining. In addition to discounting small areas the Corps of Engineers report does not include reserves below 1,500 feet nor bituminous coals less than 24 inches thick nor lignite less than 48 inches thick. The U. S. Geological Survey, however, includes reserves to a depth of 3,000 feet and includes bituminous coal 14 inches or more in thickness and lignite 30 inches or more in thickness. Reserves calculated by Corps of Engineers were less than half as much for most states and approximately 18 percent as much for the entire United States as similar calculations by the U. S. Geological Survey (11). The Corps of Engineers report in 1952 estimated 170 billion tons of recoverable reserves, and the U. S. Geological Survey in 1953 estimated 950 billion tons. Ayres and Scarlott in 1952 (12) in their discussion of energy sources of the world briefly summarize coal resources and other possible energy sources.

STRATIGRAPHY AND SEDIMENTATION

Some papers cannot be discussed conveniently by state because they are of broader geographic extent or contain theories which extend beyond state boundaries. Among the papers that fall into this category are a series by Potter, Siever, and others (183–186, 213, 215) that discussed the source of Pennsylvanian sandstones in the Eastern Interior Basin. By means of statistical analysis of crossbedding data the authors showed that the sands must have come from a northeasterly direction rather than from Llanoria to the south.

Wanless reviewed the kinds of Mississippian, Pennsylvanian and Permian

cycles of sedimentation that occur in the United States (271) and discussed in greater detail those that occur in southwestern United States (264). Cross and Arkle described similar cyclical accumulations of the Pennsylvanian and Permian in the Appalachian area (66, 67). Weller reviewed theories of origin of cyclothems (272) and discussed in more detail the diastropic control theory, which he favors. Wheeler and Murray presented a theory of cyclothemic sedimentation (274) based on four stages (in contrast to the two-phase, transgression-regression cycle). They correlated their four cyclic phases with Simpson's solar radiation glacial cycle.

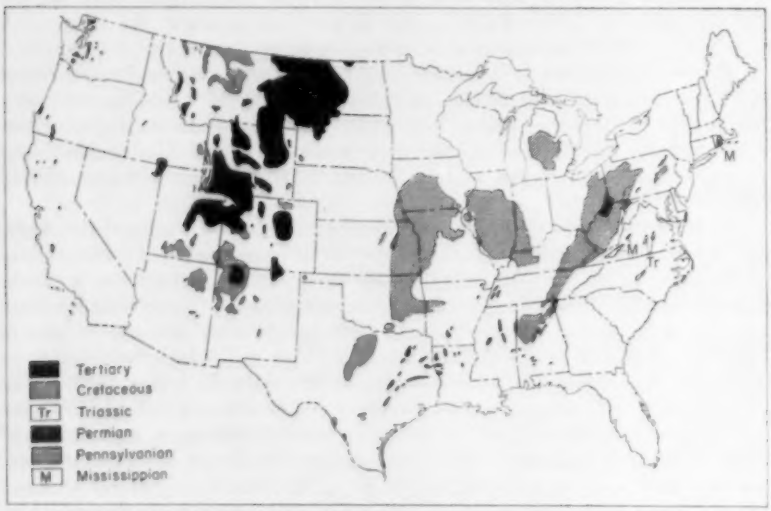

FIG. 1. Map of the United States showing generalized geologic distribution of coal.

A review of the geographic and stratigraphic distribution of Pennsylvanian rocks in the United States was made by Wanless (265). He also reviewed in greater detail all available information on the Pennsylvanian rocks of the Eastern Interior Basin (268). A reclassification of Des Moinesian rocks was agreed to by representatives from Iowa, Kansas, Missouri, Nebraska, and Oklahoma (204). The organizations represented are to be congratulated for this simplification and standardization of stratigraphic terminology. Also in the mid-continent region Moore and Mudge reclassified some upper Pennsylvanian and lower Permian rocks (172). In the Great Basin the Eastern Nevada Geologic Association compiled a revised correlation chart covering units from Cambrian to Cretaceous (105). The U. S. Geological Survey has now accepted the Pennsylvanian as a system instead of a series of the Carboniferous System (36). Series names accepted by the U. S. Geological Survey are Lower, Middle, and Upper. In the mid-continent region only, Morrow, Atoka, Des Moines, Missouri and Virgil Series will be used.

STRATIGRAPHIC AND RESOURCES STUDIES BY STATE

Alabama.—Coal occurs in the Warrior, Cahaba, Coosa, and Plateau fields in Alabama in the southern end of the Appalachian region. The Warrior field occupies a broad shallow basin; the other fields lie in structural troughs or synclines. The coals are Pottsville in age and bituminous in rank. A small amount of Tertiary lignite occurs in the southern half of the state. Alabama ranks 8th among the states in annual coal production. More than 13 million tons per year was produced from 12 counties in 1955; more than 884 million tons was produced prior to that year.

The northeastern part of the Coosa coal field has been studied by the U. S. Bureau of Mines and the U. S. Geological Survey in cooperation with the Alabama Geological Survey. It was hoped that the Coosa coal field could supply a sufficient amount of coal for railroad, industrial, and domestic markets and thus conserve the high grade metallurgical coal in the Warrior field to the west which contains the principal coking reserves of Alabama. The Bureau of Mines did some diamond drilling and worked mostly on the petrography, chemical properties, and washability characteristics of coals (233). The Geological Survey studied geology and coal resources (192).

The Coosa Basin is a shallow syncline, the southeastern limb of which is cut longitudinally by several high angle thrust faults that mark the southeast borders of the coal basins. The bottoms of the coal basins are cut by traverse faults, many of which branch from the longitudinal faults. They have affected mining adversely by tending to limit the individual operations to the fault block in which mining was begun.

The coals occur in the upper 2,000 feet of the Pottsville Formation (Pennsylvanian), which in this area is 5,500 feet thick. Fourteen of the 20 or more coal beds are thick and extensive enough to mine and have been named. Reserves were calculated on only 7 of these beds. Coals more than 20 inches thick contain 19 million tons of bituminous coal. Two-thirds of this amount is in the Fairview bed in the Fairview Basin. An additional 11 million tons was calculated for coals from 14 to 19 inches thick (192).

Alaska.—Coal deposits are scattered throughout Alaska. They have been found as far north as the Arctic coast near Point Barrow, as far southwest as Herendeen Bay on the Aleutian Peninsula, and as far southeast as Admiralty Island near Juneau. The coal ranges in age from Carboniferous to Tertiary and in rank from lignite to anthracite. Current annual production is somewhat in excess of a half million tons.

During World War II large amounts of coal were needed by the Army, the Alaska Railroad, and other agencies vitally concerned with the war effort. Both the U. S. Geological Survey and the U. S. Bureau of Mines had field parties in south-central Alaska to provide immediate information on useable coals. During the past several years the various investigations have continued and some have been completed and final reports published. Current emphasis is on Tertiary coals in the southern part of the Matanuska Valley, the Nenana, and the Bering River coal fields. The first two mentioned fields contain the only active commercial coal mines in Alaska and have been the

most intensively studied. Three reports are concerned with the Wishbone Hill district of the Matanuska coal field, an area of about 10 square miles (16, 17, 18). The total production for this district through 1952 was about 3 million tons of bituminous coal. Remaining reserves of 102 million tons of high-volatile B bituminous coal are about equally divided between indicated and inferred. These coals occur in the Chickaloon Formation (Tertiary) which is 5,000 feet thick. This formation also contains some subbituminous coals near Eska in the Matanuska coal field (143). The U. S. Bureau of Mines drilled several diamond drill holes in this coal field which, in conjunction with other available information, enabled the geologists to map in some detail the stratigraphy and structure of this area.

Reserves of 95 million tons of strippable lignite have been calculated in the Nemana coal field (250) in an area of 24 square miles. Reserves are calculated on 5 continuous coal beds 5 to 30 feet thick and a discontinuous bed that locally is 60 feet thick.

The Bering River coal field, an area 21 miles long and 2 to 5 miles wide, has not been studied in the same detail as the others, but considerable information is available (15). Anthracite and semibituminous coals occur in the Kushtaka Formation (Tertiary) in an area of complex faulting. This means that before mining can begin detailed work must be done in order to delimit areas where mining can be done economically. A few of these beds are more than 40 feet thick but in most places the coals are only a few feet thick. Preliminary work, however, has shown that the thickness of each coal varies greatly in a short distance.

Arizona.—A small amount of subbituminous coal occurs in the Black Mesa, Pinedale, and Gallup coal fields. Bituminous coal occurs in the Deer Creek field and in a small area in Apache County in the extreme northeastern part of the state. All of the coal is of Cretaceous age, and most of the seams occur in the Dakota Sandstone, the Mesaverde Formation, or the Mancos Shale. Coals in most of the area are less than 14 inches thick, except for local thickening, but in the Black Mesa field subbituminous coal seams are as much as 11 feet thick. This field contains nearly all of the state's coal reserves. The Deer Creek field contains several thin bituminous seams some as much as 30 inches thick and the field accounts for only a half of 1 percent of the state's coal reserves. The Gallup coal field, which extends into New Mexico, is of very little commercial importance in Arizona. The field is discussed briefly in a guidebook for the San Juan Basin (32). Total coal reserves for the state are probably more than 15,000 million tons, but the production in 1955 was less than 9,000 tons.

Arkansas.—The Arkansas coal field is about 85 miles long and 40 miles wide in the west central part of the State (179) and occurs in the southern part of the Western Interior region. The coal field contains low-volatile bituminous coal of Pennsylvanian age, extends westward into Oklahoma, and consists of separated and isolated basins wherein the coal has been preserved from erosion in synclines. Small isolated areas of lignite are present in eastern Arkansas but lignite is not being mined. Annual production is approxi-

mately a half million tons from 4 counties. Stratigraphic information on Morrow and Atoka (Pennsylvanian) rocks is included in some of the reports on oil well drilling (155). The rock of the Morrow and Atoka Series have been studied by Henbest (127) from the standpoint of outcrop stratigraphy and paleontology and by Ballard (14) from the standpoint of subsurface stratigraphy. A total of 96 million tons of coal has been produced in Arkansas; the production in 1955 was 600 thousand tons.

California.—Coal has been reported from 18 counties in California in rocks of Cretaceous, Eocene and Miocene age (144). Reserves of 100 million tons are estimated for lignite, subbituminous, and bituminous coals. Production in 1955 was nearly 8 thousand tons.

A discussion of coal is included in a report on the resources of Amador County (55). Here the lignite occurs in the Ione Formation of middle Eocene age, is lenticular shaped, and ranges from 1 foot to 14 feet in thickness. Montan wax is being made from this seam.

Colorado.—Coal occurs in scattered areas throughout Colorado and underlies about 25,400 square miles or 24 percent of the State. Most of it occurs in intermontane structural basins where the coals crop out around the edges and dip toward the center. Because the coals are considerably deeper in the middle of these basins, most of the exploratory work and all of the mining are done around the edges. Coal occurs in rocks of Late Cretaceous and early Tertiary age and ranges in rank from subbituminous to anthracite. By 1955 mines in Colorado had produced more than 490 million tons of coal, had an annual production of 3½ million tons from 18 counties, and ranked 11th among the coal producing states.

The U. S. Bureau of Mines has done considerable work in Gunnison County, Colorado, in an attempt to find a suitable coking coal which would have more coking strength than the Lower Sunnyside coal from Utah. Diamond drilling was done in the Coal Creek district (236) and in an area south of Dry Fork of Minnesota Creek (234). Each drilling showed from 3 to 6 high-volatile bituminous coal beds, each more than 4 feet thick and all occurring in the Mesaverde Formation (Upper Cretaceous). In the Coal Creek district reserves of 121 million tons were calculated from 3 coals. These coals are suitable for metallurgical coke as used in western blast furnaces. In the Dry Fork area 781 million tons of reserves were calculated, but the coke from these coals is considered inferior to that now being made from the Sunnyside seam.

The U. S. Geological Survey also expended considerable manpower in the state. Four publications (139, 296, 297, 299) include maps that show distribution and structure of main coals in Las Animas and Huerfano Counties in south central Colorado. Most of the coals studied are in the Vermejo Formation (Upper Cretaceous); a few coals are found in the Raton Formation (Paleocene). In the La Veta area, Huerfano County, some of the coal being mined is nearly 14 feet thick; the average thickness of the coal mined is 7 feet. The coals range in rank from high volatile A to high-volatile C bituminous coal. In northwestern Colorado in Routt and Moffat Counties

(20) most of the coals occur in the Mesaverde Group, but a few seams are found in the Lance Formation (Upper Cretaceous) and the Fort Union Formation (Paleocene). Most of the coal is bituminous or subbituminous, but small amounts of anthracite and semianthracite are present locally in an area where coal has been metamorphosed by thick sills of basalt. In southwestern Colorado (19) bituminous coals occur in the Dakota Sandstone, the Menefee Formation of the Mesaverde Group and the Fruitland Formation, all of Cretaceous age.

A preliminary appraisal of the coal reserves of Colorado was completed as of January 1952 (222). The original reserves of Colorado are estimated to be 100,408 million tons, of which 9,437 million tons is subbituminous, 90,258 millions tons is bituminous, and 713 million tons is anthracite or semianthracite. If one assumes 958 million tons mined and lost in mining remaining reserves are 99,450 million tons. Most of the coals occur in intermontane structural basins. Because little is known about the occurrence of coal in the central parts of these basins reserves were not calculated for this area. The data used to compile the estimates were restricted for the most part to mapped and explored areas within 6 miles or less of the coal outcrops. Thus the reserves include only 5,277 square miles or 20 percent of the potential area and are those coals under less than 3,000 feet of overburden. Reserves are listed by county, by field, and by rank.

Recent stratigraphic work (56) seems to confirm previous opinions that the unconformity found at the base of the Dakota Sandstone and overlying the Burro Canyon Formation separates Lower and Upper Cretaceous. In other stratigraphic studies Pennsylvanian rocks in Colorado have been studied and correlated with those in Kansas and Oklahoma (154, 159, 160, 273).

Idaho.—Small areas are underlain by coal in the St. Anthony field in the eastern part of the state, in the Goose Creek field in the center of the southern border of the state, and in the west central part of the state. Most of the coal is less than 14 inches thick and occurs in rocks of Cretaceous or Tertiary age. The coals are lignite, subbituminous, or bituminous in rank.

The Horseshoe Creek district, Goose Creek field, is the most important area from the standpoint of past mining. Approximately 100,000 tons of coal have been produced from this district since 1903 (148). The coals are found in the Frontier Formation (Upper Cretaceous), range in thickness from a few inches to 10 feet, and range in rank from subbituminous to bituminous. Additional work has been done on uranium-bearing coal and carbonaceous rocks in the Fall Creek area (246). These rocks are in the Bear River Formation of Early Cretaceous age.

Illinois.—Coals in Illinois occur in the Eastern Interior Basin, which includes southwestern Indiana and western Kentucky. The coal is found in rocks of Pennsylvanian age which, in Illinois, are divided in ascending order into Caseyville, Tradewater, Carbondale, and McLeansboro Groups. Approximately 50 individual coal beds occur in the 2,600 feet of Pennsylvanian rocks, but the commercially important beds are found in the middle 700 feet of rocks mostly in the Carbondale Group but also in the lower part of the

McLeansboro and the upper part of the Tradewater Group. The coal ranges in rank from high-volatile bituminous A to C. Nearly 46 million tons of coal were produced from 35 counties in 1955; in that year Illinois ranked 4th among the coal-producing states. Prior to 1955 nearly 3,376 million tons of coal had been produced in the State. Only two states have produced more than Illinois.

Since 1949, the Illinois Geological Survey has made great strides in its continuing program of mapping subsurface coal geology in the counties in the southeastern part of the state. This program began in 1942, when personnel from the Survey staff began to observe oil-drilling operations and to collect samples and interpret them. More than 240 such oil tests were observed, some only to the Herrin (No. 6) or to the Harrisburg (No. 5) coals and the remainder were logged through the entire Pennsylvanian. After a large number of the holes had been logged, members of the Coal Division of the Illinois Geological Survey began using the records and other information in detailed subsurface maps of selected counties. Since 1949, reports have been published which include Franklin (49); Marion and Fayette (211); Clay, Edwards, Gallatin, Hamilton and Richland (52); White (124); Shelby and Moultrie (100); Jasper (286); Wayne (102); Wabash (54); and Crawford and Lawrence (181) Counties. Key beds were emphasized in these reports.

A key bed, as used here, is a lithologic unit, commonly a coal or limestone, whose identity is reasonably definite over large areas and thus the position of other less widespread beds can be defined conveniently in relation to this bed. Correlations were made on the basis of key beds, structure maps were made on them, and in some reports isopach maps were constructed between two key beds. The key bed used in all reports is the Herrin (No. 6) coal and its caprock, the Herrin limestone. Other commonly used ones which lack the widespread distribution of the No. 6 coal are the Millersville limestone, the Shoal Creek limestone, the West Franklin limestone, and the Harrisburg (No. 5) coal. Other less commonly used key beds are No. 7 coal, No. 4 coal, No. 2 coal, and No. 2A coal. Several other studies supplemented, or were supplemented by, these coal studies. A detailed investigation of the Mississippian-Pennsylvanian unconformity made by Siever (212) was based on both surface and subsurface data.

Dubois (101) studied the relationship of structure and sedimentation in central Illinois, and Potter (182) described breccia and small-scale overthrusting in southern Illinois. In 1952 the Illinois Geological Survey published a report reevaluating the minable reserves of the state (53). More than 1,077 square miles of coal had already been mined. Twenty-one coals listed in four categories (proved, probably, strongly indicated, and weakly indicated) accounted for the 137,329 million tons of remaining reserves. This report also provides an excellent summary of the stratigraphy of coal and limestone beds and of the coal mining in each of the 33 areas used in the calculations. It is interesting to note that of the total reserves (137,329 million tons) 4 coals made up more than 90 percent of the amount. Almost half were for the No. 6 coal, more than a fourth for the No. 5 coal, approximately an eighth for the

No. 2 coal, and slightly more than a sixteenth for the No. 7 coal. The calculated reserves compare closely to the 137 billion tons of original reserves estimated by DeWolf in 1908. A series of reports on strippable coal reserves is now in progress. The first one (217) includes coal beds that are more than 18 inches thick and that have overburden not exceeding 150 feet. Stripping possibilities and salient geologic features of 17 coal beds are discussed for Gallatin, Hardin, Johnson, Pope, Saline, and Williamson Counties.

Rubey (197) has discussed the geology and mineral resources of the Hardin and Brussels quadrangles and Wanless (269) has reported on the geology and mineral resources of the Beardstown, Glasford, Havana, and Vermont quadrangles. Wanless (270) also listed more than 500 species of invertebrate fossils collected from the rocks in these quadrangles.

Indiana.—Coal-bearing rocks of Pennsylvanian age occur in an area of 6,500 square miles in southwestern Indiana along the eastern edge of the Eastern Interior Coal Basin. These rocks are divided in ascending order into Pottsville, Allegheny, and Conemaugh Series. Most of the commercial coal occurs in the Allegheny Series, but some is found in the upper part of the Pottsville Series. The coal ranks from high-volatile A to C but most of the coal is in the high-volatile C bituminous category. Indiana ranks sixth among the states with a total recorded production of 1,070 million tons and was seventh in annual production in 1955 with more than 16 million tons of coal produced from 15 counties. A good summary of available information on the coals is given in a directory of coal producers (283).

After 1908 very little work had been published on coals in Indiana until 1950. At that time the Indiana Geological Survey, in cooperation with the U. S. Geological Survey, published the first in a series of Coal Investigations Maps. Since 1950 four additional maps have been published. Each map covers one 7½-minute quadrangle at a scale of 1:24,000 and includes an areal geologic map, an economic map, a columnar section, a cross section, a text, and tables. Detailed stratigraphy and economic geology are discussed and the commercial coals are emphasized. Extent lines and mined areas for each commercial coal are shown in color on the economic map and information about drilling, active and abandoned mines, and coal reserves is shown in tables. The Jasonville (275), Linton (276), Dugger (150), Hymera (282), and Shelburn (248) quadrangles have been published. The major coals discussed are Coals III, IV, V, VI, and VII, all in the Allegheny Series.

A series of county maps called Preliminary Coal Maps are published by the Indiana Geological Survey. Six of these maps, covering Vigo (277), Sullivan (280), Pike (281), Gibson (111), Vanderburgh (112), and Clay (136) Counties, have been published since 1952. These maps show extent lines and mined areas on the major commercial coals in each of these counties and the names of all abandoned underground mines and all active mines in each county are listed on the back of the map. The maps, published on a scale of 1:126,720 (2 miles to 1 inch), include coals in the upper Pottsville and in the Allegheny Series.

Field work necessary to complete these two kinds of maps has provided considerable additional information on the correlation of some limestones and

coals and on problems of sedimentation. One particularly well developed channel sandstone coal cutout has been described (113). Murray described a depositional cycle commonly found which contains 2 coals, one developed on marine underclay and the other on nonmarine (174). Other publications include a brief discussion of coal in Parke County (285) and in the Coal City and Switz City quadrangles (151).

Coal reserves were calculated in the several individual quadrangle and county reports, but in 1953 (221) the coals in the entire state were reevaluated. Reserves in 13 counties were calculated for Coals I, Lower Block, Upper Block, Minshall, II, IIa, III, IV, IVa, V, VI, Lower Millersburg, Upper Millersburg, and VII. The reserves were divided into strippable and nonstrippable coal based on a 40-, 60-, or 90-foot overburden range; this range depended on thickness of coal and mining conditions. Original reserves of 37,293 million tons and remaining reserves of 35,806 million tons were calculated. Only 3,524 million tons of the original amount (less than 10 percent) is strippable. Approximately 75 percent of the current production is produced by stripping.

It is interesting to note that this report, which was quite conservative in the inclusion of inferred coal, estimated 37,293 million tons of coal, whereas Ashley in 1909 estimated, in a generalized and certainly not conservative manner, 46,864 million tons of coal. Ashley's errors in assuming greater than average thickness over county-size areas were somewhat compensated by the later inclusion of coals in the deeper part of the basin for which Ashley had no information.

Kansas.—All the coal mined in Kansas today is Pennsylvanian in age and occurs in the Western Interior region. Production comes mainly from the Southeastern Kansas field, the Osage field, and the Levenworth field. Coal also occurs in and has been mined from rocks of Permian and Cretaceous age. At least 53 coal seams, ranging in rank from lignite to high-volatile A bituminous coal, underlie an area of more than 18,000 square miles. Coal production in 1955 was slightly more than 740 thousand tons from 6 counties; prior production was slightly more than 275 million tons.

Coal resources of the Permian System in eastern Kansas have been summarized by Schoewe (198). The total potential reserves in Wabannsee County are nearly 13 million tons of bituminous coal. This tonnage includes both the coal more than 30 inches thick and a seam which averages 13 inches in thickness. At least 6 different coals of Permian age occur in other counties, but they are very thin and discontinuous. Only 10,000 tons of Permian coal has been mined.

A study of the coal resources of the lignite coal in the Dakota Formation (Cretaceous) in central Kansas has been completed by Schoewe (200). He discussed the geographic distribution, stratigraphic position, thickness, and physical and chemical character of the coals. He calculated 198 million tons of reserves in coals 12 to 36 inches thick. More than 300,000 tons has been mined. Adding the reserves from Permian and Cretaceous rocks to those calculated previously from Pennsylvanian rocks, one gets 20,774 million tons of remaining reserves for the state.

Several reports have been made on the Pennsylvanian stratigraphy and on the coal reserves of Kansas prior to 1949. The stratigraphy of the Pennsylvanian System has received additional study. A summary of present knowledge and interpretation has been presented by Moore and his fellow workers (170, 171). Wagner and Harris (249) have mapped the outcropping Pennsylvanian rocks in the Fredonia quadrangle, Mudge (173) has described many channel sandstones in upper Pennsylvanian and lower Permian rocks, and Miller (167) has studied marine phosphatic nodules which occur in lower Virgilian Series (Pennsylvanian) in Douglas County.

Kentucky.—Coals in Kentucky occur in two fields. One is in eastern Kentucky in the Appalachian coal area and the other is in the western part of Kentucky in the Eastern Interior Coal Basin. All the coals occur in rocks of Pennsylvanian age. In general the coals in western Kentucky are high-volatile bituminous in rank and those in eastern Kentucky are high- to medium-volatile bituminous coals. More than 2,300 millions tons was produced in Kentucky prior to 1955. In 1955, nearly 43 million tons of coal was produced from 30 counties in eastern Kentucky and more than 26 million tons from 9 counties in western Kentucky. The state ranks third in annual coal production and 4th in total amount of coal produced.

As part of its continuing program of finding and evaluating coking coals, the U. S. Bureau of Mines investigated Floyd (93), Harlan (258), Knott (95), Letcher (257), Perry (261), and Pike (89) Counties in eastern Kentucky and estimated a total of 11,776 million tons of coking coal. These coals are suitable for coking, but much of the coal must be blended with higher rank coals in order to produce high quality metallurgical coke.

The U. S. Geological Survey has completed studies of the Buckhorn (223), Campton (41), Cannel City (106), Cornettsville (142), Hyden (141), Troublesom (295), and White Oak (2) quadrangles all in eastern Kentucky. These are all 15 minute quadrangles published on a scale of 1:62,500 except the White Oak which is a 7½ minute one published at a scale of 1:24,000. The results of detailed mapping are shown by extent lines and isopach thickness lines, mined areas, and structure contours on selected coals. A short text discusses stratigraphy of the rocks and coal mining, and tables show coal analyses, reserves, and correlations. The Kentucky Geological Survey has published similar maps for the Paintsville (125) and the Prestonsburg (126) quadrangles.

Very little geologic work has been done on the coal-bearing rocks of western Kentucky in recent years. Some discussion of Pennsylvanian rocks and structure maps on top of No. 9 coals have been included in reports which are primarily on oil and gas (35, 251).

Maryland.—The coals in Maryland occur in a 400 square mile area in the western part of the state in the Appalachian area and are all Pennsylvanian in age. Nearly all of the coal occurs in five basins: Georges Creek, Upper Potomac, Castleman, Upper Youghiogheny, and Lower Youghiogheny. The coals range in rank from medium-volatile to semianthracite. Production of coal from the state has steadily declined since 1926. The decline has been

caused principally by the depletion of the Pittsburg and Sewickley beds in the Georges Creek Basin and of the Upper Freeport coal in the Upper Potomac Basin. The total coal production in the state before 1955 was nearly 263 million tons. Coal production in 1955 was slightly more than a half million tons from two counties.

Diamond drilling was done by the U. S. Bureau of Mines in Allegany and Garrett Counties in order to find additional suitable coals (235). The 10 deeper coals over 18 inches thick in Georges Creek and Upper Potomac Basins were estimated to have 600 million tons of reserves. The Castleman Basin which has not been developed extensively, was found to have 5 persistent coals in the Conemaugh and 6 coals in the Allegheny Series (237). More than 232 million tons of low- and medium-volatile bituminous coals were calculated for 6 of these coals, 14 inches or more thick. Reserves of coking coal in Allegany County 28 inches or more thick are estimated at 556 million tons (254).

Pennsylvanian rocks in Garrett County have been studied in connection with water resources studies (5), a study was made of refractory clays (247) and some revision of the Pennsylvanian-Permian boundary has been suggested (27).

Michigan.—The coal fields of Michigan are on the east side of the Michigan Coal Basin and cover an area of 11,500 square miles. The coals, which are in the Saginaw Formation of Pennsylvanian age are high-volatile B and C bituminous. These coals occur sporadically in isolated beds that vary greatly in thickness and generally pinch-out within relatively short distances. Although more than 46 million tons of coal has been produced from the State, current production is insignificant.

Reserves were calculated for Michigan as of January 1950 (58). Because there is little assurance that coal beds in Michigan extend beyond the areas of detailed information, satisfactory estimates of the extent and average thickness of the coal beds are possible only for relatively small areas. In preparing estimates of Michigan coal reserves, therefore, only those areas having adequate test-hole information were considered. No estimates were given for a large part of the Michigan Coal Basin where coal should be present, but where specific information is lacking. The estimate, which was, therefore, quite conservative shows an original reserve of 297 million tons and a remaining reserve of 220 million tons in all categories.

The oldest known coal was found in Michigan in 1949 (243). This anthracitic partially graphitized coal occurs in the Michigamme Formation of upper Huronian age (Precambrian). It is found as lenticular bodies concordantly bedded with the shale. The carbon probably came from algal remains.

Missouri.—The coal deposits of Missouri are in the Western Interior region in the northwestern part of the State and are found in rocks of Pennsylvanian age which dip gently toward the northwest. The coals range in rank from subbituminous A to high volatile A bituminous and range from less than a foot to more than six feet in thickness. Only 17 of the known

25 coal beds have been mined, and most of the production comes from the Weir-Pittsburg, Tebo, Bevier, Mulky, Lexington, and Mulberry beds (201). More than 272 million tons of coal has been produced from the state, and more than 3 million tons of coal was produced in 1955.

Special studies in Carroll and Livingston Counties have been completed (133). Two coal beds of minable thickness were mapped, and 1.7 million tons of reserves were calculated for the Croweburg coal overlain by less than 30 feet of cover. Special attention has been given in two papers to the stratigraphy of the Upper Marmaton and Pleasanton Groups (57, 132). The classification of the post-Cherokee Pennsylvanian has been revised to conform more nearly to the revised classifications used in Iowa, Kansas, and Nebraska (118). Other reports on coal are included in studies of the geology of Boone County (244), the geology of Bowling Green quadrangle (156), and Pennsylvanian rock exposed in the Kansas City area (117).

Montana.—The coal fields in Montana cover 51,300 square miles in the Great Plains and the Northern Rocky Mountain provinces. Coals in the Fort Union Formation of Paleocene age account for more than 90 percent of the reserves. Coals also are found in the Tullock and Wasatch Formations of Tertiary age, in the Kootenai Formation (Lower Cretaceous), and in the Eagle Sandstone, Judith River, and Hell Creek Formations (Upper Cretaceous). Montana, which is second only to North Dakota in total coal reserves, has produced more than 175 million tons (59) and in 1955 had a production of slightly more than a million tons each of bituminous coal and of lignite from 10 counties.

The first of a series of state coal-reserve studies being undertaken by the U. S. Geological Survey was completed for Montana in 1949 (59). Reserves of 222,046 million tons were calculated. These reserves consisted of 87,533 million tons of lignite, 132,151 million tons of subbituminous and 2,362 million tons of bituminous coal. In a general way lignite is in the eastern part of the state, subbituminous is in the north-central and south-central parts, and bituminous coal is along the west side of the north-central part of the State.

More recent studies of the lignites in the Coalwood coal field (45) and the Girard coal field (187) have been published. The coals are in the Fort Union Formation. Subbituminous and bituminous coals in the Morrison Formation have been mapped in the Stanford-Hobson area (245). Studies have been made for strippable coal in central Rosebud County (146), Custer and Powder River Counties (43), an area west of the Yellowstone River (70), and the Wibaux area (165). A small amount of work has been done on the Cretaceous coals and Tertiary coals and carbonaceous shales for uranium (82, 121).

New Mexico.—The coal fields in New Mexico are in several areas totalling approximately 14,650 square miles. The important Raton field is on the margin of the Great Plains, the San Juan River region is in the Colorado Plateau province, and a number of smaller fields lie in intermontane basins in the southern Rocky Mountain province and in the adjacent Basin and

Range province. The coal-bearing formations range in age from Pennsylvania to Tertiary. The principal economic coals, however, are of Upper Cretaceous and Tertiary (Paleocene) age. Coals range in rank from subbituminous to anthracite but the greater portion of the reserves are of subbituminous rank. Approximately 124 million tons of coal has been mined since 1882, and the production in 1955 was slightly more than 200 thousand tons.

Original reserves are estimated as 61,754.6 million tons of coal (189), of which 82 percent is subbituminous, and, except for less than 6 million tons of anthracite, the remainder is bituminous. Remaining reserves on January 1, 1948 were 61,516 million tons. Because the Pennsylvanian coal beds are commonly thin and impure and because little information about them is available, reserves were not calculated for these coals.

Four maps covering the Kirtland (23), the Naschitti (178), the Toadlena (303), and the Ship Rock and Hogback (22), quadrangles were published by the U. S. Geological Survey on a scale of 1:62,500. The maps show the crop lines of coals in the Dakota Sandstone and in the Menefee, Fruitland, and Crevasse Canyon Formations, all of Cretaceous age.

The U. S. Bureau of Mines investigated coking coals near Cerrillos, Santa Fe County (242), but determined that the coke produced was not as good as that being obtained from the Sunnyside bed in Utah. Coal of Cretaceous age was discussed by Allen and Balk (4) in a report on the Fort Defiance and Tohatchi quadrangles. Sedimentation and tectonics of Upper Pecos Valley during Pennsylvanian time have been discussed in some detail by Sidwell and others (210).

North Carolina.—Coal in North Carolina underlies an area of 150 square miles and occurs in Triassic rocks in narrow structural basins which trend northeastward. The largest of these basins and the only one that contains commercially important coal beds is the Deep River Basin. This coal basin has been studied in detail by Reinemund (190) and by Toenges and others (238). Most of the coal is bituminous, but in the western part of the coal-bearing area the coal has been metamorphosed to anthracite. Total coal production to date has been a little more than a million tons. Present reserves are estimated to be 110 million tons of which more than 90 percent is in the Cumnock coal bed and is between 3 and 4 feet thick.

North Dakota.—Lignite deposits underlie the western part of the state in an area of 35,000 square miles. The coals increase in rank westward and grade into subbituminous coals in Montana. The greatest number and the thickest coals occur in the Tongue River Member of the Fort Union Formation, and a few thin coals are found in the Ludlow Member also in the Fort Union Formation (Paleocene) and in the southwestern part of the state in the Hell Creek Formation (Upper Cretaceous). The Golden Valley Formation (Eocene) and the White River Formation (Oligocene) also contain small amounts of lignite. Individual seams range from a few inches to more than 40 feet in thickness. An excellent summary of the major geologic features of the lignites has been reported by Roe (191). North Dakota has a larger coal reserve than any state in the Union, but it has produced only 83 million

tons of coal and in 1955 it ranked 13th in annual coal production with slightly more than 3 million tons.

The U. S. Geological Survey has studied and described lignites in Slope and Bowman Counties (147, 169), Corson, Dewey and Ziebach Counties (81) and the Wibaux area (165) and has calculated reserves for the state (37). Reserves are estimated at 350,910 million tons. This calculation includes only 80 percent of the coal area or the 28,000 square miles where beds of lignite are more than 2½ feet thick. The U. S. Bureau of Mines has maintained in Grand Forks a staff who has studied lignitic coals for years. A recent publication discusses lignite in North Dakota from the standpoint of occurrence, properties, mining, preparation, storage, transportation, and utilization (46).

Lignites from the Fort Union Formation from scattered areas in the state were studied for uranium (82). Deformation of the Fort Union Formation near Lignite has been studied in some detail (239).

Ohio.—Coals in Ohio underlie 12,350 square miles in the eastern part of the state in the Appalachian region. These coals are mostly Pennsylvanian in age and bituminous in rank. The Pennsylvanian rocks in Ohio are divided into the Pottsville, Allegheny, Conemaugh and Monongahela Series. Coals occur in each series. Coals in the Allegheny Series account for more than half of the coal in Ohio. Approximately 1 percent of the reserves are in Permian coals. Coal production in 1955 was nearly 38 million tons from 25 counties and Ohio ranked fifth in coal production among the states. It also ranked fifth in the amount of total production with 1,874 million tons.

The Ohio Geological Survey has published a series of six reports on the coal reserves of Ohio since 1952; a seventh is in preparation. These reports are compiled for each coal on a state-wide basis. Each report covers the general stratigraphy of the coals and adjacent rocks, discusses one or more coals in detail and gives original reserves. Mined areas are not measured. Reserve calculations are complete for most of the major coals. They are Meigs Creek No. 9 (218), Redstone No. 8A, Pittsburg No. 8 (79), Harlem, Anderson, Wilgus, Mahoning (78), Upper Freeport, Lower Freeport, Middle Kittanning (39), Lower Kittanning No. 5 (38), Clarion No. 4A, and Brookville No. 4 (80). This latest appraisal on these coals shows 43,855 million tons of original reserves (40). This is approximately half as much as estimated by Clark in 1917 and more than three times that estimated by Ray in 1929. Clark used 14 inches as the lower limit of measurable coal reserves but Ray used a thickness of 2.7 feet and thus his results are not comparable.

Several miscellaneous papers concerning the stratigraphy of the coal-bearing rocks in Ohio have been published since 1949. One of these discusses the origin and distribution of the Sharon conglomerate, a basal Pennsylvanian formation (114). Others include a discussion of stratigraphy of beds adjacent to the Pittsburgh coal in the Federal Creek field (216), a detailed discussion of the stratigraphy and economic geology of Perry County (109), a description of a newly found fossiliferous member in the Allegheny Formation (229), and a description of fusulinids from Pennsylvanian rocks (219). An unusual publication was the Ohio Geological Survey's Open File Report No. 1 (226,

227). This is an unfinished manuscript on the Monongahela Series on which Dr. Wilber Stout had been working for a number of years before his retirement. Although a number of township discussions have not been completed, a majority of the manuscript is in good form, and it contains a tremendous amount of valuable and useful geologic information, mostly concerning surface stratigraphy. This Open File Report is not for sale, but it has been distributed to interested geology departments, geological surveys, and libraries. The administration of the Ohio Geological Survey should be commended for making this report available.

Additional discussion of Pennsylvanian stratigraphy is included in the geology of Coshocton (152) and Tuscarawas (153) Counties, and a proposal for modification of stratigraphic nomenclature was made from a study of rocks in parts of Holmes, Stark, and Tuscarawas Counties (115).

Oklahoma.—The bituminous coals of Oklahoma underlie an area of nearly 15,000 square miles in the eastern third of the State and occur in the Des Moines and Missouri Series of Pennsylvanian age. These coal-bearing rocks are continuous with those of Arkansas to the east and of Kansas to the north and are included in the Western Interior Coal Basin. A small area of coal of Pennsylvanian age is present in the south-central part of the state in Carter County, and a thin impure bed of lignite of Cretaceous age is present in the western part of the state in Cimarron County. The total amount of coal mined in the state has been more than 170 million tons. The production for 1955 was slightly more than 2 million tons from 13 counties.

Original reserves of 3,673 million tons and remaining reserves of 3,245 millions were calculated in 1953 (241). Of the remaining reserves 65 percent is high-volatile bituminous, 13 percent is medium-volatile bituminous and 22 percent is low-volatile bituminous coal. The medium- and low-volatile coals occur in the southeastern part of the coal area and are used for making coke.

Coals were discussed by the Oklahoma Geological Survey in geologic reports for Haskell (175) and LeFlore (149) Counties. In a report on the Lake Classen area, Dunham (104) notes five distinct mountain-making pulsations which began in Middle Pennsylvanian and ended in Permian or later time.

Oregon.—About 600 square miles in Oregon is underlain by known coal-bearing rocks, all Tertiary in age. The southwestern part of the state includes about 75 percent of this area and contains the Coos Bay field, the most important in the state from the standpoint of production and reserves. Here lignite, subbituminous B or C, and a small amount of bituminous coals of Eocene age are found. In other parts of the state lignite and subbituminous coals are found in beds of Eocene, Oligocene, and Miocene age. Nearly 3 million tons of coal has been produced since 1850. Current annual production is approximately 1,000 tons.

The only recent geologic work done was in the Coos Bay coal field (103). Here coals were mapped in the Coaledo and Umpqua Formations of Eocene age. The principal coal bed ranges from 4 to 8 feet in thickness. Informa-

tion is inadequate to calculate reserves for much of the remainder of the state. Reserves of 66 million tons, mostly of subbituminous C coal, represent an area of less than 11 square miles (163).

Pennsylvania.—Coals in Pennsylvania underlie an area of 15,000 miles in the Appalachian region and are Pennsylvanian in age. Most of the coal is bituminous and is in the western part of the state but a smaller part is anthracite and is in eastern Pennsylvania. The state ranked second in annual coal production in 1955 with nearly 86 million tons of bituminous coal from 26 counties and 26 million tons of anthracite. Total production in the years before 1955 was 7,834 million tons, the largest amount produced from any state.

The U. S. Geological Survey has published as part of their Coal Investigations Map series 9 reports covering the Western Middle Anthracite field in eastern Pennsylvania. These maps, on a scale of 1:12,000, show coal outcrops, structure contours on a particular coal, an explanatory text, and diagrams. The reports cover parts of the Mount Carmel (193, 194, 195, 196), Ashland (122, 123), Shenandoah (75, 145), and Delano (164) quadrangles.

The U. S. Bureau of Mines has published 11 county reports for Allegheny (256), Armstrong (90), Cambria (87), Clarion (33), Fayette (92), Greene (263), Indiana (88), Jefferson (94), Somerset (255), Washington (262), and Westmoreland (91) Counties in southwestern Pennsylvania. These reports discuss the known coking coals and estimate the reserves of coking coals more than 14 inches thick to be 17,234 million tons.

The Pennsylvania Geological Survey has been mapping coal areas in detail. They have published maps of the New Florence (206, 208, 209) and Donegal quadrangles (207), of southern Somerset County (109) and of parts of Clearfield and Elk Counties (34). These maps have been published on a scale of 1:62,000 on a topographic base. Stratigraphy of the local area is discussed and structure contours are drawn on an important coal for each map.

Other papers include a summary of available information on bituminous coal reserves (7), a report on reserves of anthracite not obtainable because of water (6), and a report on the proposal of a new type section near Pottsville for the Pottsville Formation and the Tumbling Run, Schuylkill and the Sharp Mountain Members (298).

South Dakota.—The lignite field in South Dakota covers an area of 7,700 square miles in the northwestern part of the State. The coal beds are in general flat lying, and most of the thicker beds occur in the Ludlow Member of the Fort Union Formation (Paleocene). Coal also is found in the Tongue River Member of the Fort Union Formation and in the Hell Creek Formation (Upper Cretaceous). A very small amount of bituminous coal occurs in minable quantity in the southwest corner of the State. It is high-volatile bituminous and occurs in the base of the Lakota Sandstone of the Inyan Kara Group (Lower Cretaceous). The total coal production of the state has been approximately 1 million tons, and the production in 1955 was less than 26,000 tons from 1 county.

An appraisal of the lignite resources of South Dakota was completed by

the U. S. Geological Survey in 1952 (44). Original reserves of 2,033 million tons and remaining reserves of 2,031 million tons of lignite were reported. In addition to these reserves, nearly 11,000 tons of bituminous coal were estimated.

Since these reserves were calculated more detailed geologic maps have been completed in the Cave Hills and Table Mountain areas (83), in the Slim Buttes area (84, 168), and in the Bar H area (302), all in Harding County. The maps show crop lines and mined areas of coal and the local structure. The U. S. Bureau of Mines also has done work on the South Dakota lignites. A mineral atlas (47) includes a summary of all pertinent data available on mines and mineral deposits in the Black Hills. Coal and coal-bearing rocks are covered briefly in this report.

The South Dakota Geological Survey has started a program of mapping the areal geology of 15 minute quadrangles that contain coal. They have completed and published at a scale of 1:62,500 at least 24 of these maps. Worthless Creek (72), Gopher (73), Firesteel Creek (74), and Morristown (225) quadrangles are typical of this series. Other quadrangles published are Bison, Black Horse Butte, Buffalo, Cash, Chance, Coal Springs, Date, Ellingson, Glad Valley, Govert, Harding, Haynes, Isabel, Lemmon, Lodgepole, Ludlow, Meadow, Reva, Redig, and Thunderhawk. Stratigraphic studies on the Pierre Shale (62) and on Permo-Pennsylvanian formations (21) have been completed and the Uraniferous coal beds in Perkins County have been studied (82).

Tennessee.—Coals in Tennessee underlie an area of 16,000 square miles in the Appalachian region in the eastern half of the state. The coal is Pennsylvanian in age and bituminous in rank. Small scattered areas of Tertiary lignites occur in the western end of the state. Prior to 1955 the total production from the state was 352 million tons. The state ranked ninth in annual coal production in 1955 with a 7 million tons produced from 18 counties.

The U. S. Bureau of Mines has published county reports for Bledsoe (292), Campbell (293), Claiborne (130), Fentress (157), Grundy (128), Hamilton (131), Marion (290), Morgan (294), Overton (288), Putnam (287), Scott (291), Sequatchie (289), and Van Buren Counties (129) in eastern Tennessee. All of the reports discuss reserves of known recoverable coking coal and, in addition, some of the reports include information on carbonizing properties and washing characteristics. Known recoverable reserves of coking coal more than 18 inches thick are estimated to be 1,129 million tons.

A U. S. Geological Survey Coal Investigations map shows the coal resources of the Pioneer quadrangle (107). Reports of the Tennessee Geological Survey include results of exploratory drilling in the Monterey (137) and the Southern Tennessee (158) coal fields and a detailed study of the Crab Orchard Mountain area (224).

Texas.—Coal occurs in three areas in Texas. In the north-central part of the state the coal ranges in rank from subbituminous to bituminous and is Pennsylvanian in age. In the eastern part is a large area of Eocene coals

which range in rank from lignite to subbituminous coal. In the Eagle Pass area, which extends across the Rio Grande into Mexico, the coal is subbituminous in rank and Upper Cretaceous in age. The annual coal production in Texas is approximately 1 million tons.

F. B. Plummer (180) made a study of the stratigraphy and paleontology of Carboniferous and Cretaceous rocks in the Llano region, Adams and others (1) reported on Pennsylvanian sediments in the Midland Basin, and Young and Rush (300) described the shape and manner of deposition of a small Pennsylvanian bioherm in McCulloch County.

Virginia.—Coal underlies 1,900 square miles in three widely separated areas in Virginia: the Southwest field, which contains about 97 percent of the reserves of the State; the Valley fields in the Valley of Virginia; and the Eastern fields. The Southwest field contains coals in the Pottsville Series (Pennsylvanian) which range in rank from high-volatile A to low-volatile bituminous. The coals in the Valley fields are in the Price Formation (Mississippian) and are mostly semianthracite. Coals in the Eastern fields belong to the Newark Group (Upper Triassic) and are mostly medium- to low-volatile bituminous coal, but a small amount of semianthracite has been found. Virginia ranked sixth in annual coal production in 1955 with a production of 23½ million tons from 8 counties. Prior to 1955 approximately 652 million tons had been produced.

The 12,051 million tons of original reserves calculated as of January 1951 includes 11,696 million tons of bituminous coal in the Southwest field and 355 million tons of semianthracite in the Valley fields (42). Reserves for the Triassic coals in the Eastern fields were not calculated. The remaining reserves are 11,119 million tons. A summary of coal reserves also was included in a report on the mineral resources and the mineral industry of the state (228).

Washington.—Coal occurs in Washington in five small areas which extend in a northerly direction in the western half of the state. The coal ranges in rank from lignite to anthracite. Most of the coal is Eocene in age. Current annual coal production from six counties is slightly more than a half million tons. Prior to 1955 the total state production was 146 million tons. Snavely (220) completed a report on the eastern part of the Centralia-Chehalis coal district.

West Virginia.—Almost all of the state is underlain by coal-bearing rocks. Minable coals occur in all four series of the Pennsylvanian system and in the Dunkard Series of the Permian System and are bituminous in rank. West Virginia, the leading producer of bituminous coal, produced 139 million tons in 1955 and prior to 1955 ranked second in total production with 5,661 million tons.

The U. S. Bureau of Mines has calculated 26,401 million tons of known reserves of coking coal for coals 28 inches or more thick in Brook (97), Logan (230), Marion (188), Marshall (99), McDowell (252), Mercer (260), Mingo (259), Monongalia (240), Ohio (98), Raleigh (96), and Wyoming Counties (253), West Virginia.

Cross has discussed the stratigraphy, petrology, origin, and composition of the Pittsburgh coal (64) and of the other sedimentary rocks (63) in the West Virginia, Pennsylvania, and Ohio area. Cross and Schemel mapped the coals along the West Virginia side of the Ohio River Valley (68).

Wyoming.—Wyoming contains 10 major coal-bearing areas covering 40,000 square miles in rocks ranging in age from Lower Cretaceous to Eocene. Those containing most of the reserves range from the Mesaverde and equivalent Formations of Upper Cretaceous age to the Wasatch Formation of Eocene age. The coal ranges in rank from lignite to high-volatile A bituminous. Lignite occurs only in the northeastern part of the Powder River Basin and is in such small quantity that it is included in the estimates of reserves with subbituminous coal, which is found in nearly all the coal regions of the state. The highest rank coal, high-volatile A and B bituminous, is restricted to beds in the Frontier Formation of Upper Cretaceous age in the Hams Fork region. Wyoming produced nearly 3 million tons of coal in 1955 and has mined approximately 400 million tons since 1865.

Of the known or probable coal-bearing land in Wyoming 53 percent had to be omitted in calculating reserves because of lack of information (26). As this vast area is mapped and prospected, it is certain that additional coal will be discovered and that the coal reserves of the State will be increased accordingly. Original reserves are estimated to be 121,554 million tons (25), of which nearly 90 percent is subbituminous coal and the remainder is bituminous coal. Remaining reserves on January 1, 1950 were 120,754 million tons. Personnel of the U. S. Geological Survey have continued to work in Wyoming since the reserves were evaluated and have published more detail in three areas. Most of the coal in the Alkali Butte, Big Draw, and Beaver Creek fields, Fremont County, are subbituminous (231). They occur in the Mesaverde and Lance Formations (Upper Cretaceous), Fort Union Formation (Paleocene) and Wind River Formation (Eocene). Of the 593 million tons of reserves in these fields more than 80 percent comes from the Mesaverde Formation. In the Lake De Smet area, Johnson County, a coal bed that averages more than 100 feet (161, 162) in thickness and locally is as much as 200 feet thick was described. This coal is in the Wasatch Formation (Eocene), is classified as subbituminous C, and underlies an area of at least 2½ square miles. In the Spotted Horse coal field, Sheridan and Campbell Counties (177), coals occur in the Tongue River Member of the Fort Union Formation and in the Wasatch Formation and underlie an area of 725 square miles. Reserves of 12,000 million tons of lignite and subbituminous coal are estimated.

A summary of the coal industry in Wyoming and Montana was presented by Johnson (140). A study on the distribution and deposition of the Pennsylvanian and Lower Permian rocks of Wyoming (3) also was made. These rocks do not contain coal in the state.

Other States.—Some coal occurs in at least eight additional states. Approximately 160 square miles in northwestern Georgia is underlain by coal-bearing rocks of Pottsville age. Most of the coal is bituminous, but a small

amount is semianthracite. In 1955 mines in 2 counties produced slightly more than 12,000 tons of coal. The coal fields in Iowa are in the southern two-thirds of the state in the Western Interior coal basin. Approximately 345 million tons of coal has been produced from the state and the production in 1950 was 1 million tons. Coal occurs in scattered places in Nevada. It is Tertiary in age and mostly lignite or lignitic shale. A small amount of bituminous coal occurs interbedded with volcanic ash, bentonite, and shale. Coal in Louisiana and Mississippi is lignite in rank and Tertiary in age. A small amount of coal occurs in southeastern Nebraska as a part of the coal fields in Kansas, Missouri, and Iowa. Small amounts of graphitic anthracite coal of probable Mississippian age occur in Rhode Island. Although many small mines have operated on a small scale the coals are not now being mined commercially. Coal occurs in two areas in Utah in Cretaceous rocks. In the Uinta Basin the coals are bituminous in rank and occur in the basal part of the Mesaverde Formation. In the southwestern part the coal ranges rank from bituminous to semianthracite. More than 6 million tons of coal was produced from 8 counties in Utah in 1955 and approximately 229 million tons was produced in previous years. Although considerable work has been done before 1949 on the coals and coal-bearing rocks in these states no publications were found which could be included in this review.

RESEARCH POSSIBILITIES

Problems in coal geology were outlined by G. H. Cady in 1949 (50) and by the U. S. Bureau of Mines in cooperation with Bituminous Coal Research, Inc. in 1956 (48). These problems have not been solved, but work has been done on some of them. One of the biggest problems, which seems to be common to all coal-bearing areas, is the lack of good lithologic and stratigraphic information on deeper coals and other thin units in the deeper part of the basin or area. Much of the good information results from exploratory work and mining information that, because of economic reasons, is done at places where the coals are thickest and most accessible. Thus most information is concentrated in areas where the coal is shallowest, thickest, and of highest quality. Apparently time and continuing, even though spasmodic, diamond drilling can provide us with more and better information over the entire area of each basin.

In order to make mapping of coal beds more economic instead of academic the data collected should include information on variation of physical and chemical qualities and kind and distribution of impurities in the coals. Thickness and properties of coals should be related to adjacent lithologies. For instance, one might compare physical and chemical properties in coals that have underclays of marine origin with those of nonmarine origin or coals that have a marine roof with those that have a nonmarine roof. Sand-shale ratios of the part of the cyclothem that underlies a coal and local structure on the coal may indicate certain properties in a coal.

New geophysical methods should be developed for finding coal, for de-

termining its extent and thickness, and for determining its iron-sulfide content. Self-potential, resistivity, and velocity measurements seem to offer the best possibilities.

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RELATIONSHIP OF CARBONATE CEMENT TO LITHOLOGY AND VANADIUM-URANIUM DEPOSITS IN THE MORRISON FORMATION IN SOUTHWESTERN COLORADO[1]

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ABSTRACT

Carbonate content was determined for 888 samples from the Salt Wash member of the Morrison formation in the Slick Rock and Uravan mining districts in southwestern Colorado. The carbonate content of most samples was determined semiquantitatively by calculating the amount of calcite equivalent to the mass of carbon dioxide evolved when the samples were treated with 3 normal hydrochloric acid. The content of some samples was determined in the course of standard chemical assays and the content of others was visually estimated.

Samples were assigned to categories or "rock types" on the basis of gross lithology, vanadium-uranium content, degree of epigenetic alteration, and degree of oxidation through weathering. The average carbonate content was determined for each rock type, and the distribution of carbonate around oxidized and unoxidized ore was investigated.

Results indicate that sandstone in the uppermost (ore-bearing) part of the Salt Wash member contains 2.5 to 3.0 percent carbonate, whereas sandstone in the lower (generally barren) part of the Salt Wash member contains about 13 percent carbonate. Altered mudstone in the Salt Wash member contains about 4 percent carbonate, and unaltered mudstone about 7 percent.

Carbonate-rich zones in sandstone adjacent to contacts with mudstone may be of syngenetic or early diagenetic origin, whereas carbonate-rich zones associated with ore bodies may be genetically related to the ore deposits.

Where the sandstone has been subjected to weathering, the overall distribution of carbonate does not seem to have been greatly affected.

[1] Publication authorized by the Director, U. S. Geological Survey.

INTRODUCTION

VANADIUM-URANIUM deposits in sandstone on the Colorado Plateau are now generally thought to have had an epigenetic origin, though there is no agreement as to the specific nature of the mineralizing process. Regardless of the nature of the epigenetic mineralizing process, it may have had an effect upon distribution of carbonate cement in the host sandstone, or the process itself may have been influenced by the original distribution of carbonate cement. The present study was undertaken to determine how carbonate cement is distributed in the Salt Wash member of the Morrison formation and if this distribution shows any relation to vanadium-uranium deposits in the Salt Wash.

This work was done by the U.S. Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

THE MORRISON FORMATION

The Morrison formation of Late Jurassic age is widely distributed in the Western Interior of the United States. Regional characteristics and differences have been described by Craig and others (1). This paper is concerned with areas in southwestern Colorado where the Morrison formation is divided into two members, the Brushy Basin member and the underlying Salt Wash member. The Brushy Basin member ranges from about 300 to 700 feet in thickness, and is composed of varicolored bentonitic mudstone with minor interbedded lenses of conglomerate and sandstone which are more abundant near the base of the member.

In the areas covered by this report, the Salt Wash member of the Morrison formation ranges from about 275 to 450 feet in thickness and is composed of mudstone with interbedded lenses of quartzose sandstone. The mudstone is dominantly reddish brown and the sandstone is light red to light gray or buff. Most of the carbonate within the sandstone occurs as cementing material.

The Salt Wash member can be divided roughly into three parts. At the top and bottom of the Salt Wash member, lenses of sandstone coalesce and form fairly continuous layers of sandstone that contain numerous thin layers of mudstone. The central part of the Salt Wash member is composed dominantly of mudstone containing scattered, unconnected lenses of sandstone. The three parts of the Salt Wash member interfinger and are more evident when viewed on a broad scale. Most of the significant vanadium-uranium deposits in the Morrison formation occur in the top sandstone layer of the Salt Wash member, which is commonly referred to as the "ore-bearing sandstone."

In the vicinity of vanadium-uranium deposits, the normally light-red to red-brown sandstone and mudstone are light gray to brown and gray green to yellow brown, respectively. The light-gray, brown, and gray-green colors resulted primarily from epigenetic bleaching of originally red sediments (3), though locally, where sandstone contains abundant carbonaceous material, the bleaching may have been the result of diagenetic as well as epigenetic proc-

TABLE 1. PRINCIPAL ROCK TYPES IN THE SALT WASH MEMBER OF THE MORRISON FORMATION AND THEIR CHARACTERISTIC COLORS

Rock type	Unoxidized	Oxidized
Mineralized sandstone[1]	Gray to black	Gray to black with various amounts of yellow, red, or green
Barren sandstone		
Unaltered	Light red to brownish red	Light red to brownish red
Altered	Light gray	Yellow brown to buff. Commonly with brown speckling
Mudstone		
Unaltered	Brownish red	Brownish red
Altered	Gray green	Gray green with minor yellow brown

[1] All mineralized sandstone is altered.

esses. In this study, all rocks that are shades of gray, green, or brown are considered to have been epigenetically bleached. In the subsequent discussion, these bleached rocks will be referred to as "altered" rocks. The unbleached rocks, which are shades of red, will be referred to as "unaltered."

Partial oxidation of the rocks has occurred where the Salt Wash member has been exposed to atmospheric conditions. This partial oxidation is indicated by the formation of limonite from pyrite, the formation of secondary uranium minerals, and the destruction of small amounts of carbonaceous material. In this paper, the term "oxidized" will be used to indicate rocks which, after their formation, have been subjected to the oxidizing environment of the atmosphere, but have not necessarily been oxidized so completely that all elements are in their highest valence state. According to this usage, rocks classed as oxidized may show a wide range in actual over-all oxidation state, as the term "oxidized" applies only to the epigenetic history of the rock, not to the over-all oxidation state.

It is necessary to distinguish between altered, unaltered, oxidized, and unoxidized samples, because alteration and oxidation, as here defined, may have caused significant changes in the distribution of carbonate cement. Color is a good indication of the relative degree of alteration and oxidation. Unaltered rocks are light red to brownish red, and because their components were originally deposited in a high state of oxidation, they undergo no color change when subjected to the oxidizing conditions of weathering. Despite the fact that unaltered rocks may have undergone no appreciable over-all oxidation during weathering, the weathered and unweathered varieties will be referred to as "oxidized" and "unoxidized" to maintain a consistent terminology. Altered unoxidized rocks are light gray to gray green. Upon oxidation, altered mudstone may become yellow brown, but more commonly it maintains a gray-green color. Altered sandstone, when oxidized, is yellow brown and commonly has a brown speckling. Unoxidized vanadium-uranium minerals are black; oxidized minerals are shades of yellow, red, or orange.

The rocks of the Salt Wash member can be divided into categories on the basis of particle size, vanadium-uranium content, alteration, and oxidation.

These categories will be called the "principal rock types" of the Salt Wash member. For clarification, these rock types and their characteristic colors are listed in Table 1.

METHOD OF INVESTIGATION

Samples were collected from mine workings and diamond-drill cores so that their spatial position relative to lithologic contacts and mineralized zones was known. Samples collected from outcrops or associated with oxidized ore minerals were considered to be oxidized, whereas samples collected from deep drill holes, well below the present water table, or samples associated with unoxidized ore-minerals, were considered to be unoxidized.

Quantitative data on the carbonate content of each sample was obtained by one of three methods. Chemical assays of 162 samples were made for vanadium oxide, uranium oxide, and calcium carbonate. A rapid, semi-quantitative method of analysis was adapted and used by the author to obtain data on 467 samples. Finally, estimates were made of the carbonate content in 259 samples. Each analytical method is described in a following section.

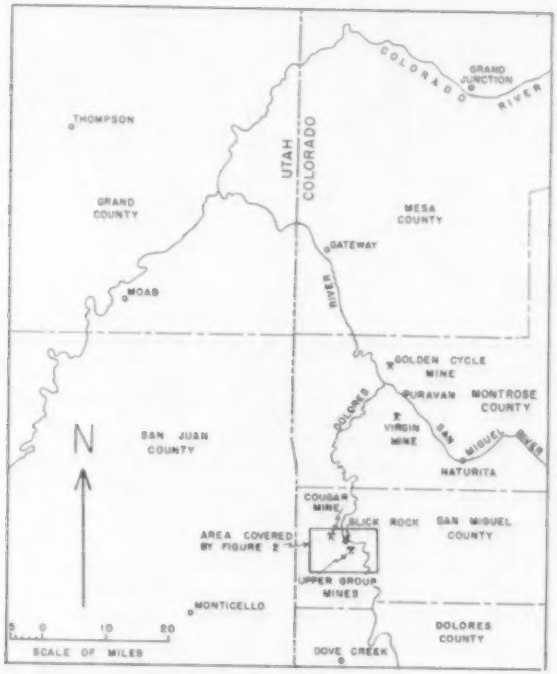

FIG. 1. Index map of part of Colorado Plateau showing localities referred to in text.

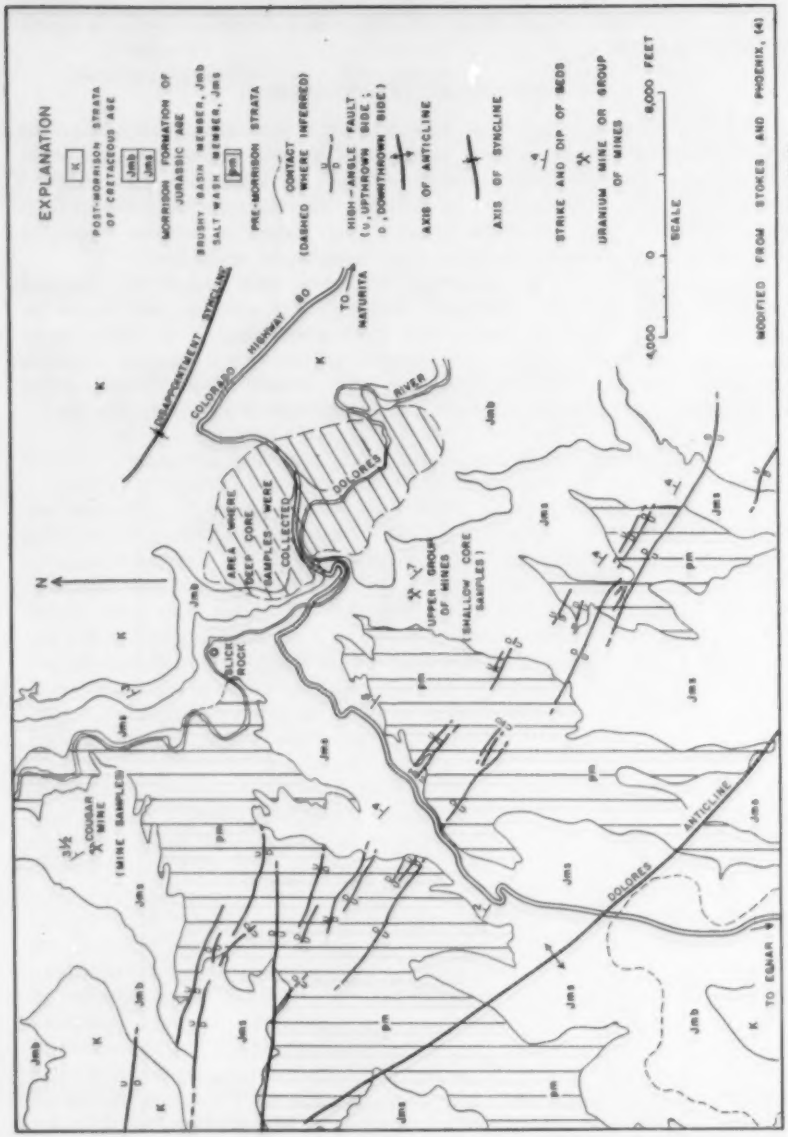

FIG. 2. Generalized geologic map of Disappointment Valley area showing sample localities.

Source of Samples.—Most of the samples for this study are from the Disappointment Valley area of the Slick Rock mining district, San Miguel County, Colo. (Figs. 1, 2), where samples were collected from mines in oxidized ore deposits and from drill cores in both oxidized and unoxidized rocks. In the Uravan mining district, Montrose County, Colo., 132 unoxidized samples were collected from the Virgin and Golden Cycle mines (Fig. 1). Table 2 shows the number of samples collected from each locality and rock type, as well as the number treated by each of the three analytical methods.

TABLE 2

NUMBER OF SAMPLES COLLECTED, SHOWING SAMPLE LOCALITY, TYPE OF SAMPLE, AND METHOD OF ANALYSIS

Sample locality	Rock type	Number of samples		Method of carbonate determination		
		Unoxidized	Oxidized	Rapid method	Chemical assay[1]	Estimation
Slick Rock district						
Disappointment Valley area	Altered barren ss	238	—	238	—	—
	Unaltered barren ss	47	—	47	—	—
	Altered mudstone	47	—	47	—	—
	Unaltered mudstone	47	—	47	—	—
	Mineralized ss	58	—	—	58	—
Upper Group mines	Mineralized ss	—	104	—	104	—
Cougar mine	Mineralized ss	—	33	16	—	17
	Altered barren ss	—	175	72	—	103
	Altered mudstone	—	7	—	—	7
Uravan district						
Golden Cycle mine	Mineralized ss	12	—	—	—	12
	Altered barren ss	44	—	—	—	44
Virgin mine	Mineralized ss	32	—	—	—	32
	Altered barren ss	44	—	—	—	44
	Totals	569	319	467	162	259

Total number of samples = 888

[1] Assays made by C. G. Angelo, G. W. Boyes, Jr., R. F. Dufour, Mary Finch, S. P. Furman, R. G. Havens, C. A. Horr, H. H. Lipp, E. C. Mallory, J. Meadows, T. Miller, J. W. Patton, L. F. Rader, D. L. Shafer, J. P. Schuch, D. L. Skinner, D. L. Stockwell, James Wahlberg, and J. E. Wilson, U. S. Geological Survey.

Methods of Analysis for Carbonate.—A rapid semiquantitative method for carbonate analysis was used to analyze 467 samples. The method, adapted from that described by Scott and Jewell (2), consisted of calculating the mass of carbon dioxide liberated when a rock sample of known weight was treated with hydrochloric acid. Analysis was carried out in three steps: first, a 100 ml. beaker containing 10 ml. of 3 normal hydrochloric acid was weighed; then a weighed sample of crushed rock (3 to 5 grams) was placed in the acid, and the resulting reaction was allowed to proceed until all effervescence stopped; finally, the beaker containing the acid solution and rock residue was reweighed and the mass of evolved carbon dioxide was calculated. The mass of calcium carbonate, and the total percentage of carbonate (calculated as calcium carbonate) in the rock sample was determined.

Inaccuracies may have resulted from 1) evaporation of acid or loss due to splattering, 2) absorption of carbon dioxide by the acid solution, 3) materials in the rock sample, other than calcium carbonate, which may have reacted with the acid, and 4) carbonates that did not react with the acid solution. The first two sources of error were reduced by rapid work, careful addition of the crushed rock to the acid, and use of a volume of acid not too much in excess of that needed to react completely with the sample. All carbonate was calculated as calcite, although locally carbonates in the Salt Wash member are dolomitic, sideritic, or ankeritic. Errors in absolute percentage of carbonate have probably resulted, but these errors are believed to be small and the effect on relative amounts of carbonate in samples from the same locality is probably negligible unless amounts of magnesium, iron, and manganese have a wide range in different rock types in the same area.

TABLE 3

CARBONATE CONTENT DETERMINED BY USING RAPID ANALYTICAL METHOD ON PREPARED STANDARDS

Actual percent carbonate (as $CaCO_3$)	Percent carbonate by rapid analytical method
0.0	0.2
0.0	0.5
1.1	1.2
2.3	2.3
4.6	4.6
5.8	5.9
7.4	7.6
8.4	8.4
8.6	8.1
10.8	9.7
14.5	14.0
15.1	14.1
21.1	20.2
33.9	34.6
100.0	102.0
100.0	102.9

Carbonates that contain appreciable amounts of iron, manganese, or magnesium react slowly with the acid and loss of weight through exaporation causes errors so large that the method cannot be used. All samples from the Disappointment Valley area reacted quite readily with the acid and the carbonate is probably largely calcite. Table 3 shows the accuracy of this method when used on standards prepared by mixing known amounts of powdered calcite and acid-washed sand. Where natural rather than artificial samples are used the errors are no doubt slightly larger, but the method seems adequate for semiquantitative work and has the advantage that analyses can be made quite cheaply and rapidly.

Standard chemical assays for uranium oxide, vanadium oxide, and calcium carbonate were made by analysts of the U. S. Geological Survey. An acetic acid leaching process was used to determine percentages of calcium carbonate. Where it has been possible to compare these determinations with those made using the rapid analytical method, the two are in close agreement.

Carbonate contents of some samples from the Cougar mine (Slick Rock district) and all samples from the Uravan district were estimated. Samples from the Golden Cycle and Virgin mines in the Uravan district reacted slowly with the acid solution and for this reason the rapid analytical method could not be used. Estimates were made by treating the samples with dilute

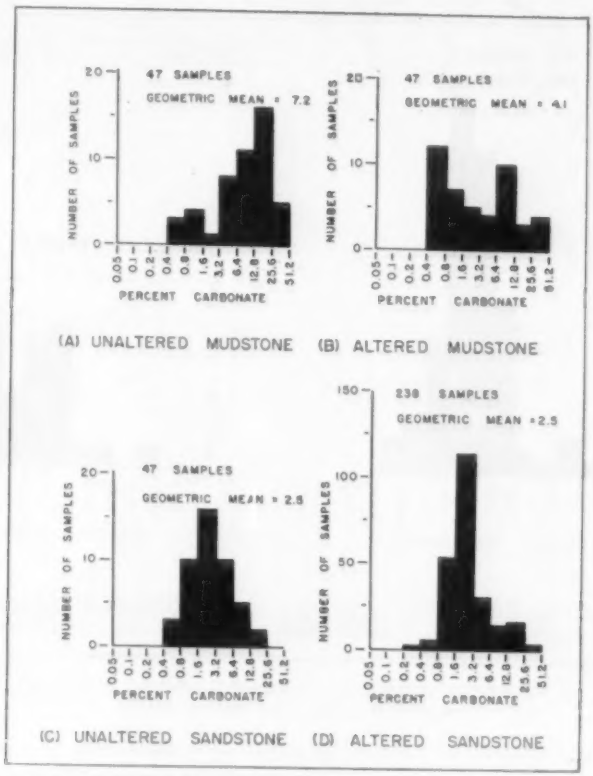

FIG. 3 Comparison of carbonate content in barren unoxidized rocks of the Salt Wash member of the Morrison formation.

hydrochloric acid then classifying the samples as containing none, trace, sparse, moderate, or abundant carbonate by the degree of effervescence. To evaluate the carbonate percentages in each of these categories, the estimated content for some samples was compared with the content determined using the rapid analytical method. Those samples estimated to contain a "trace" of carbonate contained 0.5 percent or less, "sparse" from 0.5 to 1.5 percent, "moderate" from 1.5 to 5.0 percent, and "abundant" more than 5.0 percent carbonate.

The percentages given apply only to samples from the Slick Rock district. Actual percentages were not determined for samples from the Uravan district because they reacted too slowly with the acid, probably because they contain appreciable amounts of magnesium.

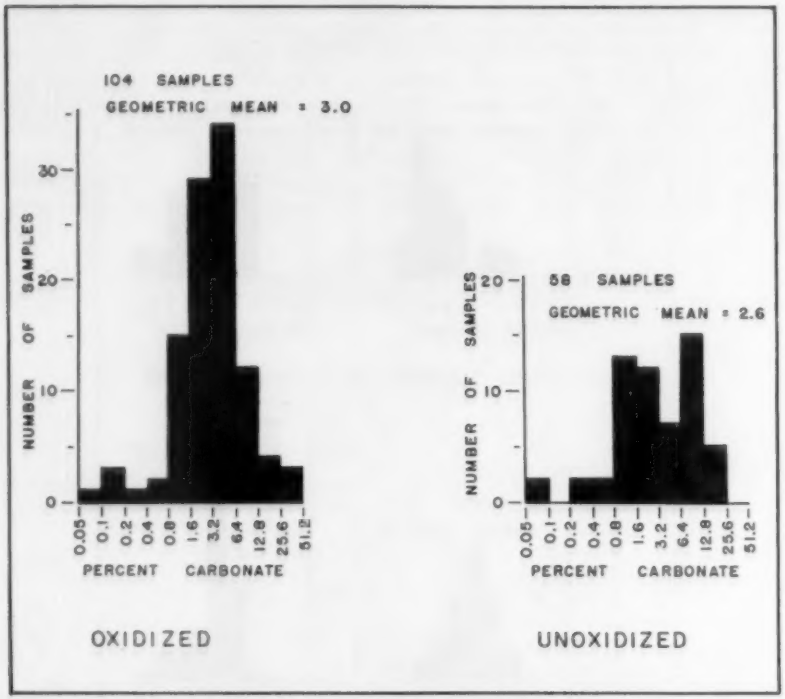

FIG. 4. Carbonate content in mineralized sandstone of the Salt Wash member of the Morrison formation.

For the purposes of comparing groups of analyses, the geometric mean has been used as the measure of central tendency because this measure minimizes the effect of a few abnormally low or high individual determinations and gives a truer average for each group.

RESULTS

Carbonate Content of Principal Rock Types of the Salt Wash Member.—Figures 3 and 4 show histograms of carbonate content for each of the principal unoxidized rock types. From the geometric mean values in Figures 3 and 4, three conclusions are drawn: 1) all types of unoxidized sandstone are similar in average carbonate content, 2) unoxidized mudstone contains more car-

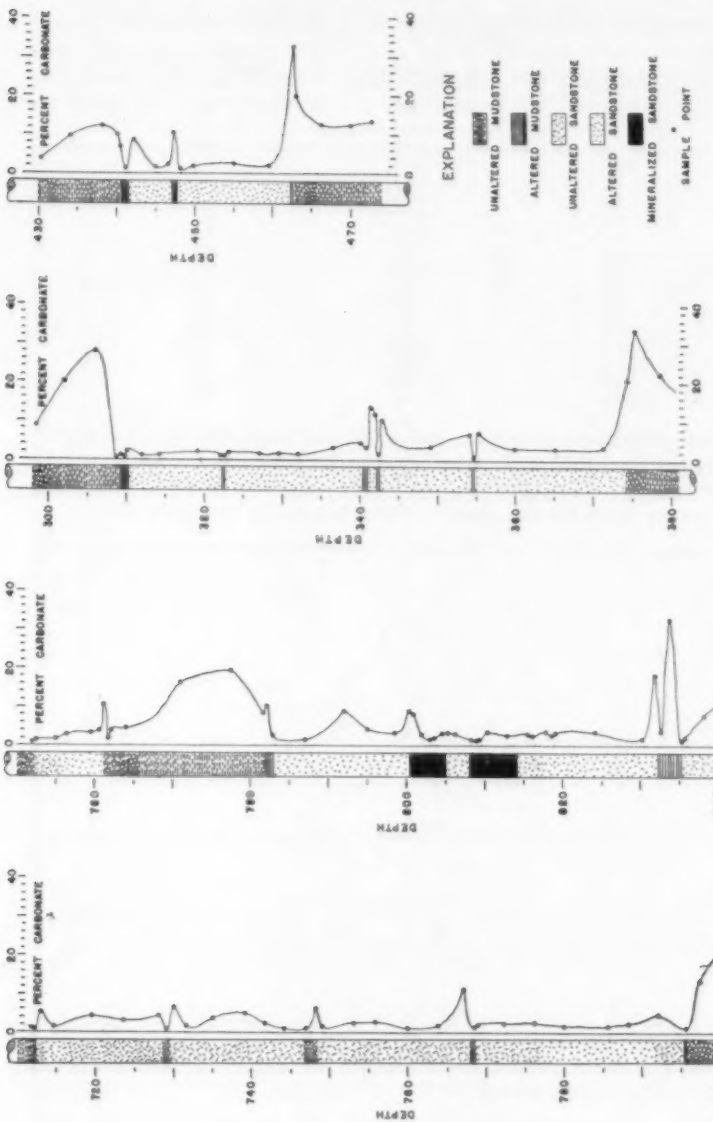

FIG. 5. Distribution of carbonate in unoxidized drill cores through top part of the Salt Wash member of the Morrison formation.

TABLE 4

COMPARISON OF CARBONATE CONTENT ON EITHER SIDE OF ALTERATION CONTACTS IN MUDSTONE

Percent carbonate in altered mudstone	Percent carbonate in unaltered mudstone	Vertical distance separating samples (in feet)
0.4	0.9	0.2
0.8	12.4	2.1
1.1	28.5	3.3
37.0	20.9	0.5
3.1	10.2	0.5
2.2	19.1	1.0
0.7	12.5	0.3
0.7	7.0	1.1
10.5	7.8	0.2
9.3	6.3	0.3
3.8	5.6	0.3
6.7	5.1	0.1
3.5	5.6	0.3
11.4	16.8	0.4
47.1	16.3	0.4
13.6	13.2	0.3
0.0	0.0	0.5

bonate than unoxidized sandstone, and 3) altered mudstone contains slightly less carbonate than unaltered mudstone, though both show a wide range in carbonate content. Limy nodules are locally abundant in altered mudstone and may be the cause for the bimodal histogram shown in Figure 3B.

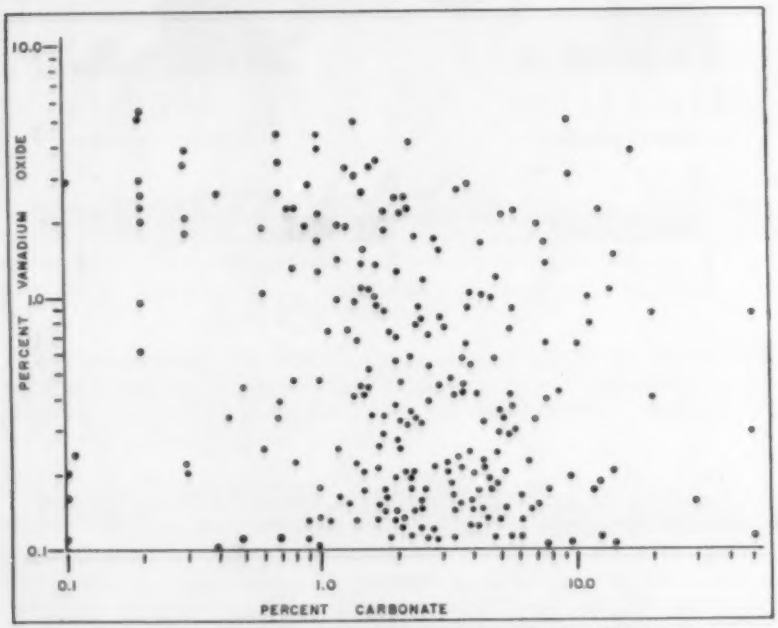

FIG. 6. Carbonate versus vanadium oxide in samples of oxidized sandstone, Upper Group of mines, San Miguel County, Colo.

Mean carbonate percentages for all types of oxidized rocks have not been determined although oxidized and unoxidized mineralized sandstone have been compared (Fig. 4). The mean values for carbonate in oxidized and unoxidized mineralized sandstone, 3.0 percent and 2.6 percent respectively, are fairly close, though there is a difference in the two distributions. Car-

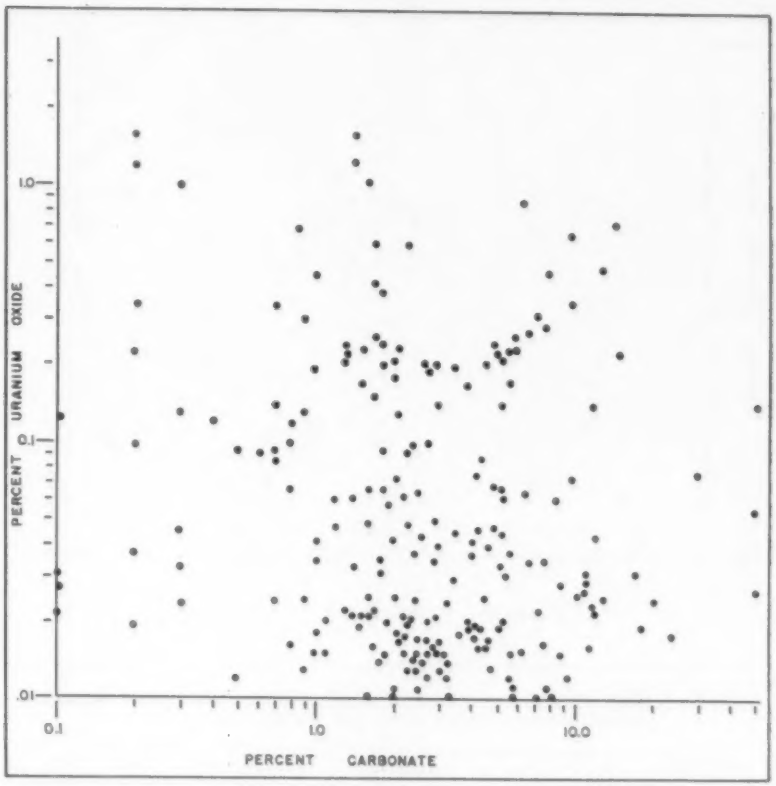

FIG. 7. Carbonate versus uranium oxide in samples of oxidized sandstone, Upper Group of mines, San Miguel County, Colo.

bonate in oxidized mineralized sandstone has a unimodal distribution, whereas in unoxidized mineralized sandstone it has a bimodal distribution. The reason for this difference in distribution is not apparent; possibly the bimodal distribution resulted from redistribution of original carbonate during mineralization, and destruction of the bimodal distribution may have resulted from slight changes during oxidation.

Estimates of carbonate content in sandstone of the lower Salt Wash indi-

cate that the lower sandstone (generally barren) contains appreciably more carbonate than the upper (ore-bearing) sandstone. This is in agreement with the work of Craig and others (1, p. 147) who report an average of 13 percent carbonate cement for sandstone of the Salt Wash as a whole.

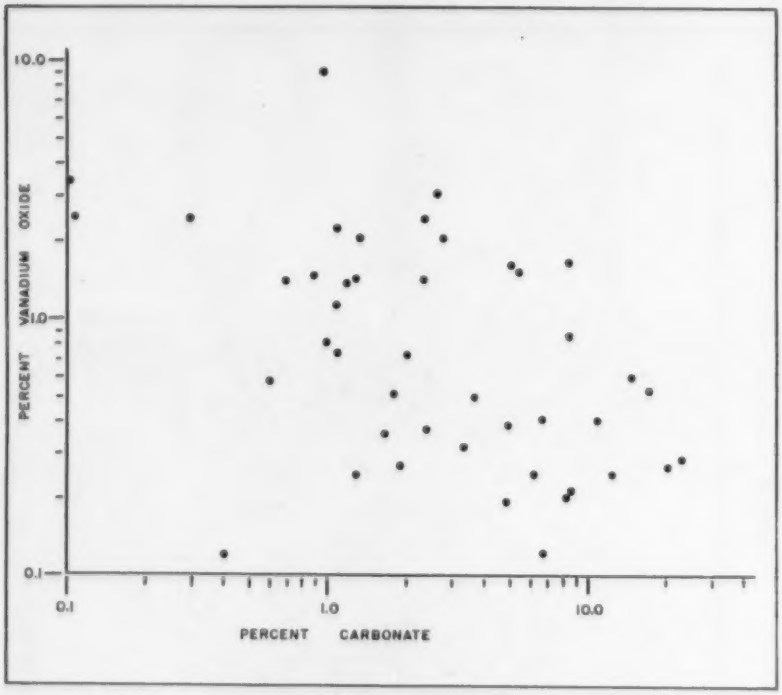

FIG. 8. Carbonate versus vanadium oxide in samples of unoxidized sandstone, Disappointment Valley area, San Miguel County, Colo.

Carbonate Distribution at Lithologic Contacts.—The carbonate content of oxidized and unoxidized sandstone is generally greatest adjacent to contacts with mudstone (Fig. 5), where, according to data obtained by Robert A. Cadigan and David A. Phoenix (oral communications, 1955), sorting and permeability in the sandstone are at a minimum.

Samples were taken on either side of contacts between brownish red (unaltered) and gray-green (altered) mudstone. At 10 of the 17 contacts sampled, the carbonate content was significantly less on the gray-green (altered) side of the contact (Table 4). At 2 contacts, there was essentially no difference in the amount of carbonate on either side, and at the remaining 5 contacts, the carbonate concentration was greater on the gray-green side.

Carbonate and Vanadium-Uranium Content.—In the Disappointment Valley area, no correlation exists between the carbonate content and the vanadium or uranium content of mineralized samples. This lack of correlation is apparent in both oxidized and unoxidized sandstone (Figs. 6, 7, 8, and 9).

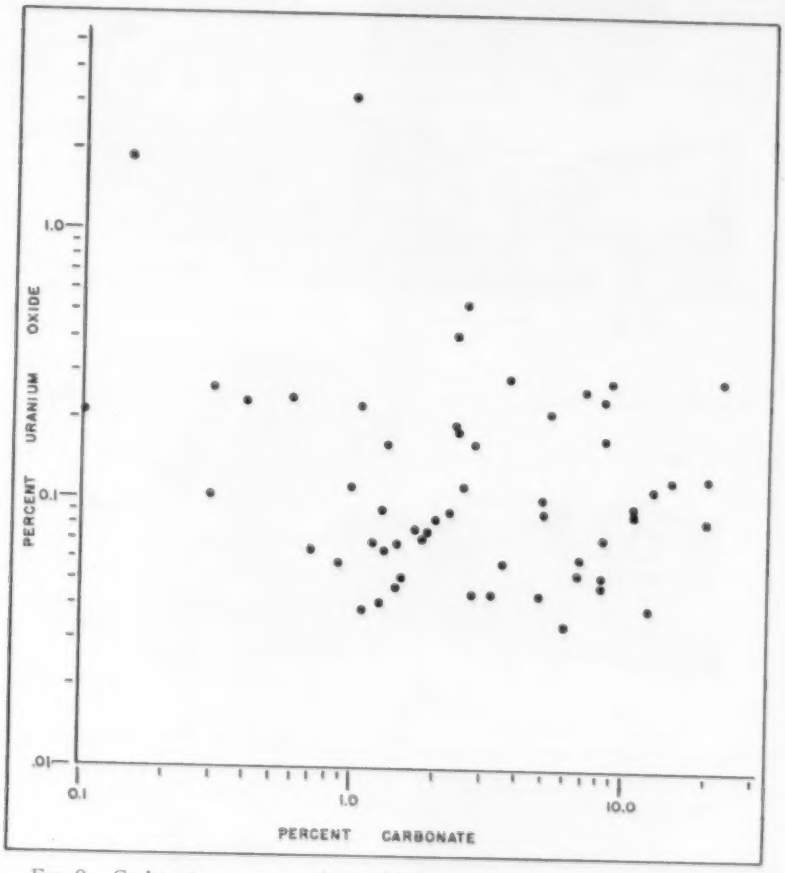

FIG. 9. Carbonate versus uranium oxide in samples of unoxidized sandstone, Disappointment Valley area, San Miguel County, Colo.

Carbonate Distribution Relative to Mineralized Sandstone.—Ore bodies in sandstone of the Salt Wash member occur in two forms: irregular tabular or lenticular masses that are flat lying but which may pinch and swell in short distances, locally cutting across the bedding; and elongate bodies called "rolls" which have curved cross sections and cut sharply across bedding. An ore

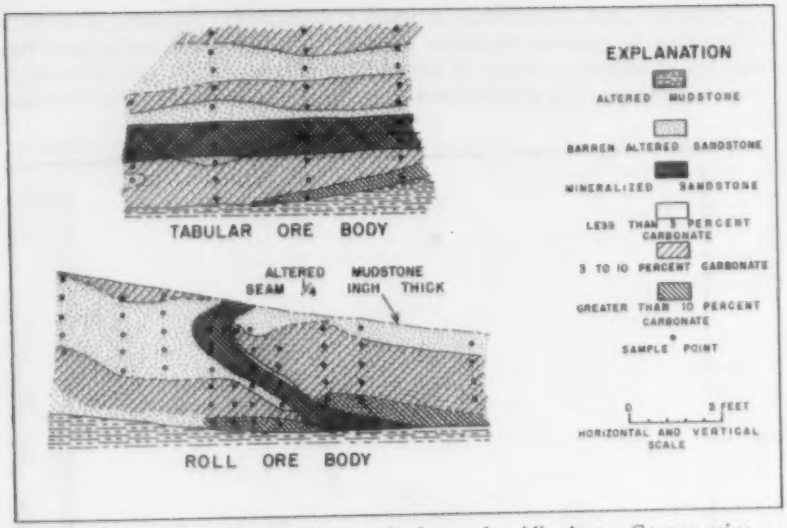

FIG. 10. Distribution of carbonate in faces of oxidized ore, Cougar mine, San Miguel County, Colo.

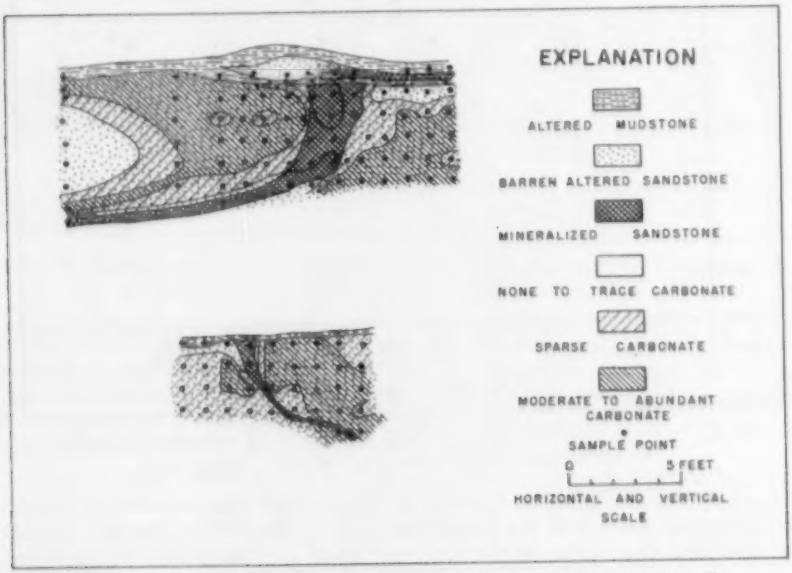

FIG. 11. Distribution of carbonate around oxidized roll ore bodies, Cougar mine, San Miguel County, Colo. (based on estimates of carbonate content).

deposit may be composed mainly of one type of ore body, but most deposits contain both types.

Samples from mines indicate that higher than average amounts of carbonate (more than 3 percent) occur in sandstone in zones close to and roughly parallel to both types of ore bodies in both oxidized and unoxidized ore deposits. Carbonate-rich layers occur above and below tabular or lenticular

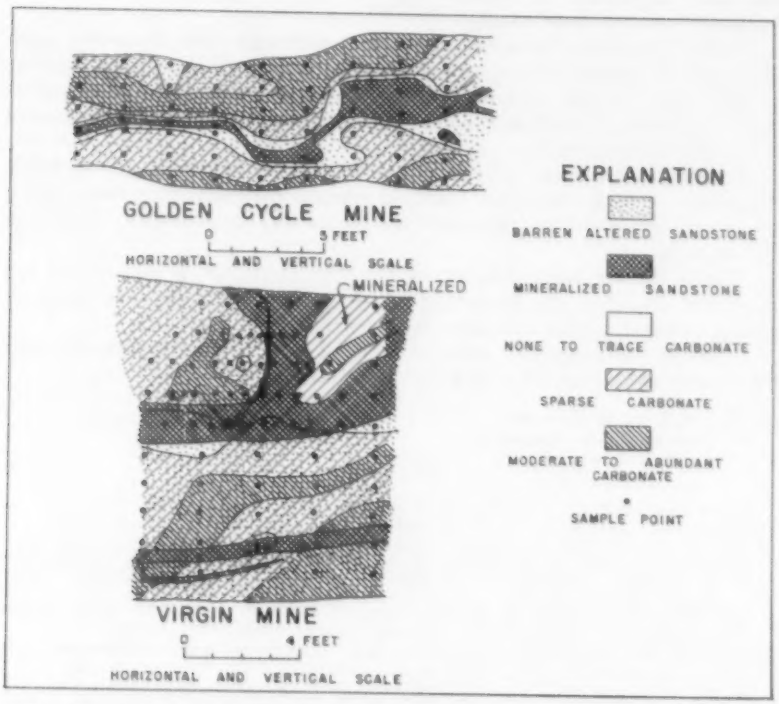

FIG. 12. Distribution of carbonate around unoxidized ore bodies, Uravan district, Montrose County, Colo. (based on estimates of carbonate content).

ore bodies; these layers are up to several feet thick and may be in contact with the ore or separated from it by several feet of barren sandstone containing average amounts of carbonate (Figs. 10 and 12). The ore contains near-average amounts of carbonate.

Carbonate-rich zones are also found adjacent to and roughly parallel to roll-type ore bodies (Figs. 11 and 12).

Carbonate-rich zones are also associated with mineralized sandstone in unoxidized drill cores (Fig. 5).

SUMMARY AND CONCLUSIONS

Sandstone from the top (ore bearing) unit of the Salt Wash member of the Morrison formation contains an average of 2.5 to 3.0 percent carbonate regardless of whether or not it has been epigenetically altered, mineralized, or weathered (oxidized). The lower (generally barren) sandstone lenses of the Salt Wash member contain several times more carbonate than those of the upper sandstone. It appears that the ore-bearing sandstone originally contained less carbonate cement.

Altered mudstone contains slightly less carbonate than unaltered mudstone and the process of mudstone alteration probably involved some leaching of carbonate. On the other hand, altered and unaltered sandstone have about the same amount of carbonate, and possibly the mudstone and sandstone were altered by different agents.

Carbonate-rich zones adjacent to contacts with mudstone are probably syngenetic or early diagenetic features, whereas carbonate-rich zones which are closely associated in space with ore bodies may be genetically related to ore deposits.

Where the ore-bearing sandstone has been subjected to weathering and associated oxidation, the average carbonate content has apparently not been greatly changed nor has carbonate been appreciably redistributed.

If certain carbonate-rich zones or types of carbonate are genetically associated with ore bodies, they might be useful as ore guides.

DEPARTMENT OF GEOLOGY,
UNIVERSITY OF MICHIGAN,
ANN ARBOR, MICH.,
Sept. 25, 1958

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GROUND-WATER PROVINCES OF INDIA[1]

GEORGE C. TAYLOR, JR.

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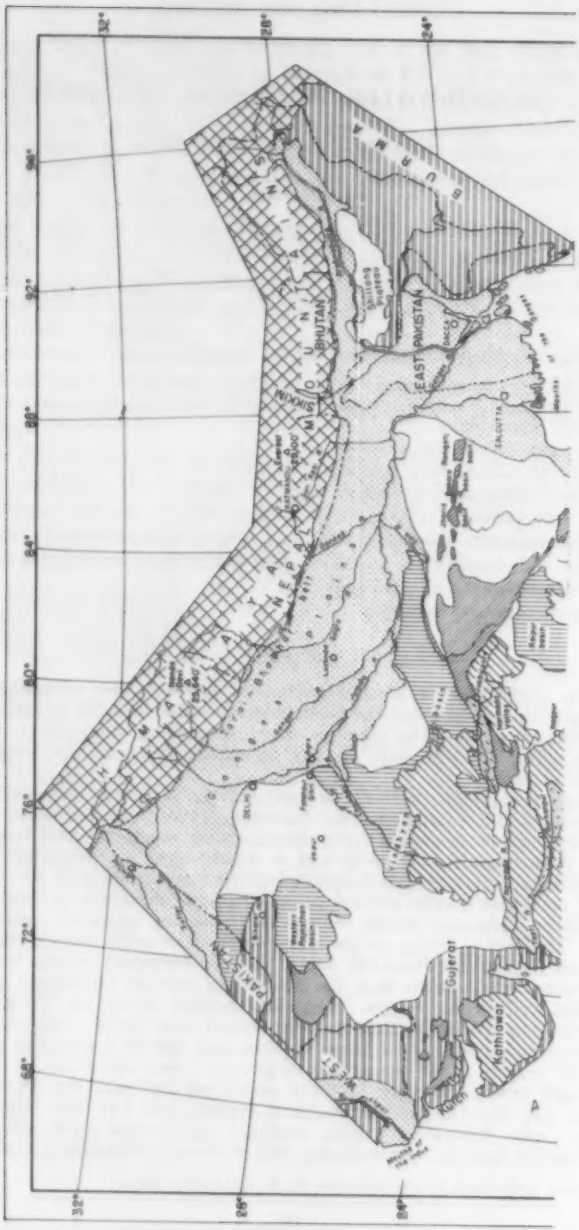
ABSTRACT

This paper gives a general resumé of ground-water utilization and development and describes the occurrence of water in eight ground-water provinces of India. The paper is based in part on observations of the writer during 1951–55 and in part on earlier work of the Geological Survey of India.

Ground water has been utilized extensively in India since before the beginning of the Christian era. Currently (1956) ground water is an important source of supply for domestic, stock, municipal, and industrial needs throughout the Republic and is widely used for irrigation in the Peninsular and Ganges-Brahmaputra regions west of longitude 85°. Dug, bored, and drilled wells are the principal means by which ground water is developed, although locally infiltration tunnels or improved springs are used. Methods of lifting or pumping water from wells include the hand line and bucket, the hand-lift pump, the counterpoised sweep, bullocks, and "mote," the water wheel, horizontal and vertical centrifugal pumps, and deep-well turbine pumps. The most common device for lifting water for irrigation is still the time-honored bullock and "mote" (leather bag). However, in modern India there is increasing use of mechanical pumps.

With respect to the occurrence of ground water, India can be divided into eight provinces, lying in three major regions, (1) the Peninsular region, (2) the Ganges-Brahmaputra region, and (3) the Himalayan region. The Peninsular region contains six ground-water provinces. Precambrian igneous, metamorphic, and indurated sedimentary rocks and

[1] Publication authorized by the Director, U. S. Geological Survey.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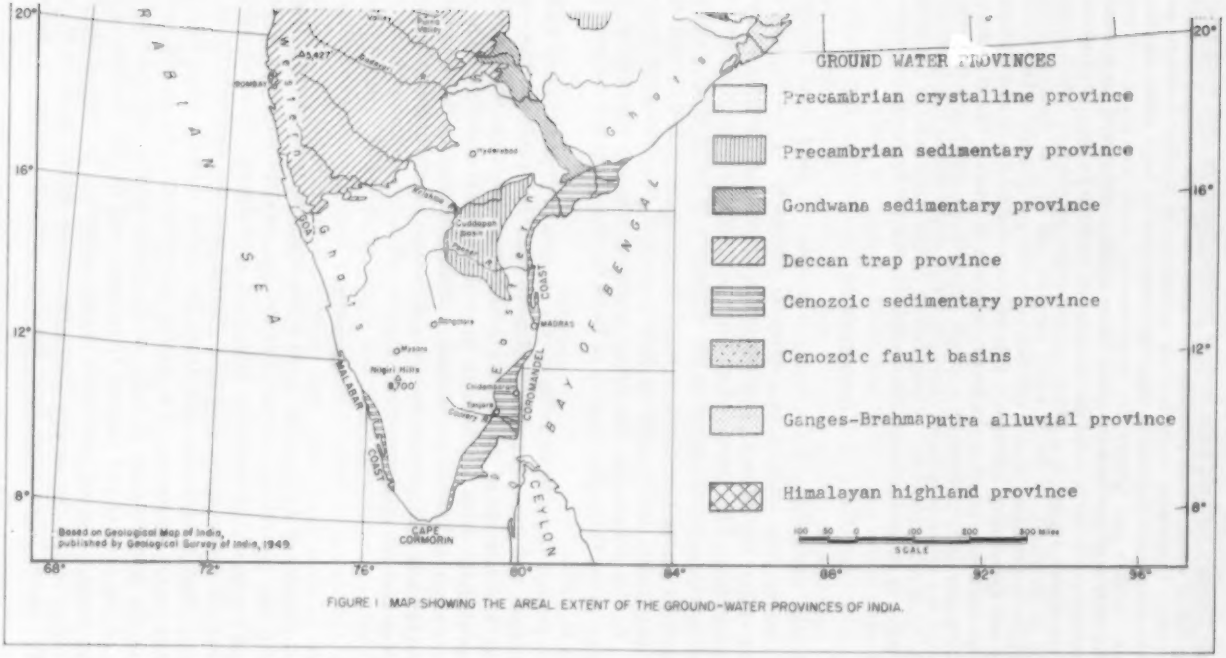

FIGURE 1 MAP SHOWING THE AREAL EXTENT OF THE GROUND-WATER PROVINCES OF INDIA.

early Tertiary volcanic rocks in three of these provinces yield many small supplies of water, which generally is of good quality but locally is brackish or salty. Cretaceous water-bearing sandstones in another province are moderately productive and in places are developed for large water supplies. Late Tertiary and Quaternary water-bearing sands and gravels in two other provinces sustain many small water supplies and several large water supplies—particularly in the coastal areas of southern India. The Ganges-Brahmaputra region is a single ground-water province in which many tens of thousands of small water supplies and several thousand large supplies are obtained from water-bearing sands and gravels in late Tertiary and Quaternary alluvium. This province constitutes a vast ground-water reservoir, which is the most productive in India. The Himalayan region also is considered as a single province, in which ground water occurs in a series of narrow valleys filled with moderately to highly permeable Quaternary alluvium. These alluvial valleys transmit large quantities of water to the ground-water reservoir in the Ganges-Brahmaputra region.

INTRODUCTION

DURING the years 1951–55 the writer, a member of the United States Geological Survey, was assigned as a technical adviser to the Geological Survey of India and in this capacity participated in several field studies of ground-water problems. This paper, which gives a general resumé of ground-water use and development and describes the occurrence of water in the eight major ground-water provinces of India, is based in part on observations made during these field studies and in part on earlier work of the Geological Survey of India. In this connection, the writer wishes to express appreciation to his colleagues of the Geological Survey of India for their help and support during his stay in India.

The present Republic of India covers an area of approximately 1,220,000 square miles and has a population of more than 320 million. The republic extends from latitude 8° to 32° north and from longitude 68° to 97° east and has altitudes from sea level to more than 25,000 feet (Fig. 1). With this wide range in latitude and altitude, India has a great diversity in climatic, topographic, and geologic environments and consequently in the ground-water conditions that are related to them.

CLIMATE

The climates of India range from arctic-alpine to tropical rainy types, all of which are controlled in large measure by seasonal winds or monsoons. Most of the annual precipitation falls from June through October, when the southwest or wet monsoon prevails. Except near the southern tip of India relatively little precipitation falls from November through May, during the northeast or dry monsoon. The annual precipitation is 80 to 150 inches or more on the western coast of India, in the Brahmaputra valley, on the lower slopes of the central and eastern Himalayas, and on the Shillong Plateau. In these areas a tropical rain-forest climate prevails. In most of the Peninsular region and in the Ganges Plains the annual rainfall is 30 to 80 inches, and the climatic types range from the drier monsoon savanna to the wetter

tropical savanna. Northwestern India has an annual precipitation of about 10 to 30 inches, and the climate of this area is that of the low-latitude steppe.

TOPOGRAPHY

The major topographic divisions of India comprise the Peninsular, the Ganges-Brahmaputra, and the Himalayan regions (Fig. 1). Most of the Peninsular region is a moderately dissected plateau whose altitude is 500 to 3,000 feet above sea level. Near the Arabian Sea and the Bay of Bengal the plateau is bordered by broken escarpments or "ghats" which descend sharply to narrow coastal plains. Elsewhere the plateau surface is interrupted by clusters of hills and elongated ridges that reach altitudes of as much as 5,400 feet in the Western Ghats inland from Bombay and 8,700 feet in the Nilgiri Hills of southern India. The Ganges-Brahmaputra region is coextensive with a lowland which stretches for more than 1,500 miles between the Peninsular plateau and the Himalayan highlands and is 50 to 200 miles wide. This lowland includes the almost level to gently sloping alluvial plains of the Ganges and Brahmaputra Rivers and their tributaries as well as the vast deltaic plains of these rivers. From sea level the surface of the lowland rises gradually to altitudes of about 800 feet near Lahore and in the upper Brahmaputra valley. The Himalayan region comprises the Himalaya Mountains and their associated foothill ranges. This highland contains the world's highest and most rugged mountains, many of which rise to altitudes of more than 25,000 feet. Deep gorges and narrow valleys, some with local relief of several thousand feet, dissect this mountainous region.

GEOLOGY

The major geologic divisions of India coincide to a marked degree with the major topographic divisions. The Peninsular region is made up very largely of early Precambrian igneous and metamorphic rocks, which constitute one of the world's great shield areas of ancient rocks. These are at or near the surface in about half the region (Fig. 1) but are veneered or deeply buried (1) by late Precambrian to early Paleozoic sediments in a number of discrete structural basins, (2) by late Paleozoic and Mesozoic sediments of the Gondwana system in a dozen or more assymetric downfaulted or downfolded basins, (3) by the great lava field of the Deccan trap whose flows cover an area of more than 200,000 square miles, (4) by Upper Cretaceous and Cenozoic sediments in an extensive embayment, five narrow coastal plains, and a folded belt, and (5) by Quaternary alluvium which fills three fault basins (Fig. 1). In addition, the Shillong Plateau forms a detached segment of the Precambrian Peninsular shield. Most of the Ganges-Brahmaputra lowland occupies a great crustal downbuckle or foredeep formed between the mobile orogenic belt of the Himalayas and the stable Peninsular shield. This foredeep is filled with upper Tertiary and Quaternary alluvium which in some areas may attain a thickness of a few thousand feet. The Himalayan region is underlain largely by sedimentary rocks of Paleozoic to Cenozoic age. These rocks

have been greatly deformed by thrust faulting and folding and in places have been metamorphosed during the orogeny of the Himalayas.

GROUND-WATER UTILIZATION AND DEVELOPMENT

Utilization.—The utilization of ground water in India dates back to times before and during the early part of the Christian era, for mention is made of wells in the great Hindu epics, Mahabharata and Ramayana. Many existing wells at ancient Hindu temples have been used for hundreds of years for ritual ablutions. For example, sacred wells at the Tanjore and Chidambaram temples in southern India reportedly have been in use more or less continuously since the twelfth and thirteenth centuries. There is also considerable record of the use of wells and infiltration tunnels (kharezes) in the sixteenth and seventeenth centuries during the period of Mogul domination. Typical is the Khara well at Bikaner, which reportedly was constructed during the reign of the Mogul Emperor Akbar (1556–1605 A.D.) and is in use still (1956). At palaces, forts, and mausoleums built by the Moguls in Agra, Delhi, Fatehpur Sikri, and other places in central and northern India many wells and a few infiltration tunnels were constructed for domestic, stock, and irrigation purposes, and some of these still exist. Other wells were used for cooling the air of subterranean living quarters to which Mogul princes and their ladies repaired to escape the scorching heat of the Indian summer. Another ground-water development of historical interest is the infiltration tunnel "Sukhar bhandar," constructed by order of the Mogul Emperor Shah Jehan (reigned 1627–1658 A.D.) near Burhanpur in central India. This tunnel, which was built originally to furnish water for the marbled baths of the Emperor's beloved, Mum-Taj, now supplies the town of Burhanpur.

Currently (1956) ground water is an important source of water supply for domestic, stock, municipal and industrial uses and for irrigation in most of the Republic. The teeming population of rural India depends in large measure on water from wells and springs for village, domestic, and stock requirements. Moreover, west of about longitude 85° (Fig. 1) in the Peninsular and Ganges-Brahmaputra regions extensive use is made of wells for irrigation of wheat, rice, millet, pulses, bananas, oranges, sugar cane, and other food and forage crops. Where the annual rainfall is about 20 inches or less, wells are in most places the chief source of water for irrigation. Where the rainfall is 20 to 40 inches, wells are used commonly for the auxiliary irrigation of crops sown during the wet monsoon or for the sole irrigation of crops sown and harvested during the dry monsoon.

The urban population of the larger cities, such as Bombay, Calcutta, Delhi, and Madras, is served principally by public surface-water supplies. However, in these cities wells also are used to supplement locally inadequate surface-water supplies and to serve the needs of many private industries. Many of the smaller cities and towns of the Republic are served entirely or partly by water supplies from wells.

Development.—Ground water in India is developed principally by means of dug, bored, and drilled wells, although locally infiltration tunnels or im-

proved springs are used. The most common type of well is the time-honored dug well. These vary from place to place in shape, size, and lining materials, according to the depth to water, the local rock type, the intended use, and the method of lifting water. Throughout India, where the water table is less than 25 feet below the land surface, shallow infiltration pits or pit wells have been constructed for the ritual ablutions of worshipers at Hindu temples. Most of the pit wells are bordered by stone- or brick-terraced slopes or "ghats" used by worshipers in their devotions. The pit wells are generally of square or rectangular shape and from 50 to as much as 250 feet wide. Wells dug for irrigation also are generally of large diameter, so as to afford maximum volume for accumulation of water and working space for pumps or bulky water-lifting devices. Irrigation wells of square, oval, or rectangular shape that are 10 to 60 feet wide are common in the Peninsular and Ganges-Brahmaputra regions, and other dug wells intended for village, domestic, or stock use are commonly of circular shape and less than 15 feet wide. Formerly, many dug wells put down for village use were connected with a narrow slot extending from the land surface to the water level. Steps were cut or set in the slot so that the village water-carrier could walk directly down into the well, conveniently perform his ablutions, and fill his water jar at the same spot. However, such "step" wells are easily contaminated, and hence their use is now discouraged by governmental authorities. The most common materials used for the linings of dug wells are rough-dressed blocks of native stone, sun- and oven-dried bricks, or concrete rings. Blocks of native stone are used for lining in most of the Peninsular region, although large-diameter wells may be unlined or only partly lined where the local country rock is cohesive. Bricks are commonly used for well linings in the Ganges-Brahmaputra region, and concrete rings are used in many areas for lining village wells.

In order to tap a greater thickness of water-bearing material and to augment yield, many dug wells are deepened by one or more 4- to 8-inch borings which are generally put down by simple hand-operated augering devices. Irrigation wells of combination dug and bored construction are particularly common in Kutch and Gujerat in western India and in the Tapti valley of central India.

Drilled wells are used increasingly for irrigation in modern India, particularly in the Ganges-Brahmaputra alluvial province, in the Coromandel coastal plain and in the Gujerat region of the Cenozoic sedimentary province, in the Gondwana sedimentary province of central and western India, and in the Cenozoic fault basins (Fig. 1). West of longitude 85° in the Ganges Plains, construction of drilled wells for irrigation has been in progress since about 1933 by the state governments of Punjab, Uttar Pradesh, and Bihar. By 1950 some 2,500 irrigation wells had been completed in these states, largely by hand- or power-percussion drilling methods. Since 1952 the Government of India has augmented the drilling program of the state governments with the financial and technical assistance of the United States International Cooperation Administration. At the end of 1956 about 3,000 wells were completed or scheduled for completion in the Ganges Plains under terms of Indo-American cooperative agreements. These wells are drilled by conventional

rotary or reverse-circulation methods. Active drilling of wells for irrigation also has been in progress since 1950 in the Gujerat region of Bombay and the Coromandel plain of Madras. By the end of 1956, about 500 wells in Gujerat and about 200 wells in the Coromandel coastal plain had been completed by State authorities using both conventional rotary and percussion drilling methods.

The methods of lifting or pumping water from wells in India include (1) the hand line and bucket, (2) the hand lift pump, (3) the counterpoised sweep, (4) bullocks and "mote," (5) the water wheel, (6) horizontal and vertical centrifugal pumps, and (7) deep-well turbine pumps. For lifting water for village or domestic use, the hand line and bucket in dug wells or the hand-operated lift pump in drilled wells are commonly used. Counterpoised sweeps with rope and bucket or leather bag, similar to the Egyptian "shadoof," are widely used in east-central and southern India for raising water for irrigation from wells or infiltration pits, where water levels are less than 20 feet below the land surface. However, throughout the Peninsular and Ganges-Brahmaputra regions the most common device for lifting water for irrigation from dug wells is the age-old combination of bullocks and "mote." This device consists of a "mote" (leather bag, usually of buffalo hide) attached to a rope which is passed over a pulley. The "mote" is raised from and lowered to the water by a yoke of bullocks or by a camel. The quantities of water obtained from single wells by this method of lift generally range from about 800 to 2,000 gallons per hour, depending on the depth to water and the activity of the well operator. Another water-lifting device widely used in northern and northwestern India is the water-wheel or "noria," which reportedly was imported into India from Persia by the Moguls. This device consists of an endless chain of earthen pots or small metal buckets extending below the water level in the well and passed over a wheel with a horizontal axis. The wheel is turned and the water is raised by a camel or yoke of bullocks which push a horizontal bar around a vertical shaft. Because of greater efficiency, the quantities of water which can be lifted by the water-wheel are somewhat more than those obtained by bullocks and "mote." Horizontal centrifugal pumps belt driven by diesel engines are extensively used for raising water for irrigation from dug or dug and bored wells in the Deccan trap province and the Tapti Valley of central India, in the Precambrian crystalline province of southern India, and in Kutch and Gujerat (Fig. 1). Most of the pumps individually produce less than 250 gallons per minute. In the Ganges Plains where pumping lifts are low, vertical and horizontal centrifugal pumps set in working pits and driven by electric motors are used in drilled irrigation wells. However, deep-well turbine pumps are used where lifts are more than about 30 feet. The pumps in the Ganges Plains are generally designed for yields of about 350 to 750 gallons per minute.

GROUND-WATER OCCURRENCE

With respect to the mode of occurrence of ground water, India can be divided into eight ground-water provinces lying in three major regions. Two of the provinces are coextensive with two of the regions (Fig. 1).

Precambrian Crystalline Province.—The Precambrian crystalline province, occupying almost half the area of India, extends discontinuously from Cape Comorin to Delhi (Fig. 1). This province is underlain by igneous and metamorphic rocks of Precambrian age, chiefly granite, gneiss, schist, slate, quartzite, and marble or variants of these. Ground water occurs in the weathered and jointed parts of these rocks—generally within 250 feet of the land surface.

The granite, gneiss, and schist are commonly weathered to depths of as much as 100 feet under the tropical climatic conditions prevailing in the central and southern parts of the Peninsular region and to depths of 60 feet or more in the semiarid northwestern part of the region. The weathered mantle of disintegrated rock or "gruss" is a large but not especially permeable ground-water reservoir. The yields of wells depend on the well diameter, the depth of penetration in saturated gruss, and the thickness and permeability of the saturated mantle. In central and southern India thousands of dug wells tap water in the gruss at depths of 25 to 100 feet below the land surface. Many of the wells used for irrigation are as much as 60 feet across, and are capable of sustained yields of 100,000 gallons a day or more. On the average, however, the dug wells less than 10 feet in diameter have sustained yields ranging from about 10,000 to 15,000 gallons per day. In northwestern India most dug wells tapping water in gruss are less than 25 feet in diameter, are less than 80 feet deep, and most have individual sustained yields of 5,000 to 15,000 gallons per day. Generally, the water in the gruss mantle of central and southern India contains less than 1,000 parts per million of dissolved solids. Locally, however, the water may be brackish or even slightly salty. On the other hand, water in the gruss of northwestern India commonly contains 3,000 parts per million or more of dissolved solids.

Slates and related rocks are important ground-water reservoirs in a large part of northwestern India. Ground water in these rocks circulates mainly in openings along joints, bedding planes, and cleavage planes, most freely where these have been enlarged by weathering. Most ground-water circulation in the slates appears to occur within 250 feet of the land surface. In northwestern India the yields of individual wells dug in slate have been found to average about 12,000 gallons per day.

The quartzites and marbles are perhaps the poorest water-bearing rocks in the Precambrian crystalline province. The openings in these rocks are not so numerous or continuous as those in other rock types of the province. Consequently, the yields of water obtained from individual wells in quartzite and marble are generally no more than a few thousand gallons per day.

Precambrian Sedimentary Province.—The Precambrian sedimentary province comprises four discrete structural basins (Fig. 1) within the Precambrian crystalline basement. These basins contain indurated limestones, sandstones, and shales and locally conglomerates, belonging principally to the Cuddapah, Kurnool, and Vindhyan systems, which are of middle or late Precambrian to early Paleozoic age.

Owing to compaction and cementation after deposition, the primary open-

ings in these sedimentary rocks have largely disappeared. The shales are relatively impervious. Moreover, systems of solution passages do not appear to have developed to an important extent in the limestones of any of the Precambrian sedimentary basins. Thus, ground-water circulation through these rocks is apparently concentrated along bedding planes and in joints or other secondary fractures, chiefly in the limestones and sandstones and locally in the conglomerates. Ground water circulates to a depth of 500 feet or more in the Precambrian sedimentary basin of western Rajasthan in northwestern India (Fig. 1) and to depths of at least 300 feet in the Raipur basin of central India and the Cuddapah basin of southern India (Fig. 1).

Many hundreds of water supplies are obtained from dug wells commonly 50 to 400 feet deep in the basin of western Rajasthan, 10 to 100 feet deep in the Vindhyan basin of north-central India (Fig. 1), and 10 to 200 feet deep in the Raipur and Cuddapah basins. The individual yields of most wells in sandstone and limestone in these basins are about 1,000 to 40,000 gallons per day, averaging about 15,000 gallons per day. In the basin of western Rajasthan the dissolved-solids content of the water is generally more than 2,000 parts per million and locally more than 5,000 parts per million. In the other three basins the water is hard but generally contains less than 1,000 parts per million of dissolved solids.

Gondwana Sedimentary Province.—The Gondwana sedimentary province comprises more than a dozen different assymetric fault troughs, grabens, structural basins, or folded belts (Fig. 1). These contain consolidated to semiconsolidated sandstone and shale in about equal proportions, a little limestone, and a basal tillite that is generally not important as a water-bearer except locally. The rocks all belong to the Gondwana system, which ranges in age from late Carboniferous to early Cretaceous and which is divided into a lower and an upper unit by a stratigraphic break in the early Triassic.

The Lower Gondwana rocks occur principally in fault troughs or grabens and structural basins in the central and east-central parts of the Peninsular region (Fig. 1). Shales, which predominate in the Talchir series of the Lower Gondwana, are generally compact and relatively impermeable. On the other hand, the sandstone members of the Damuda series are more permeable, and constitute important aquifers where they are present. For example, in the Jharia, Raniganj, and Bokaro basins of east-central India, water-bearing sandstones of the Damuda series are interbedded with coal seams and necessitate extensive dewatering operations in many mines, several of which are reported to pump a million gallons of water a day or more. Elsewhere in these and other basins many dug wells, generally less than 100 feet deep, yield individually as much as 100,000 gallons a day from water-bearing sandstone; and wells drilled a few hundred feet deep so as to tap more than one saturated stratum of sandstone may yield individually 250,000 gallons per day or more. The water in Lower Gondwana sandstones is moderately hard but generally contains less than 1,000 parts per million of total solids. Locally, the water contains considerable iron. Where coal seams are present, the water may contain hydrogen sulfide.

The Upper Gondwana rocks occur in structural basins or folded belts principally in the central, western, and northwestern parts of the Peninsular region (Fig. 1). Friable sandstones in the uppermost part of the Gondwana system generally are moderately permeable. Where present in the zone of saturation such sandstones constitute the most productive aquifers in the Gondwana sedimentary province. For example, several wells, 200 to 300 feet deep, in sandstones of the Jubbulpore series near Jubbulpore in central India have individual sustained yields of 300 to 600 gallons per minute. In the state of Kutch in western India, water-bearing sandstones in the Bhuj series of the uppermost Gondwana are tapped by several thousand dug or combination dug and bored irrigation wells. These range from about 20 to 300 feet in depth, and most of them are capable of sustained individual yields of 100 to 600 gallons per minute. The water from Bhuj sandstones in Kutch generally is very hard and commonly contains 500 to 2,000 parts per million of dissolved solids. Locally, however, the water is brackish or salty.

Deccan Trap Province.—The Deccan trap province comprises an area of more than 200,000 square miles in central and western India (Fig. 1). This province is underlain by a series of basaltic lava flows that range in age from late Cretaceous to Eocene and whose accumulated thickness is from a few tens of feet to a few thousand feet. The flows are generally flat lying or gently warped but in places they are folded or faulted.

Throughout the Deccan trap province, water occurs in the weathered and jointed parts of the rock and in openings between the lava flows. However, in contrast to plateau lavas in other parts of the world, deep circulation of ground water does not appear to take place to any important extent in the flows of the Deccan trap. A large number of borings have been put down to depths of 500 to 2,000 feet in different parts of the province, and most of these have encountered little or no water below depths of about 150 feet.

The weathered basalt, locally called "mooram," and joints and openings between flows, all enlarged by weathering, collectively constitute the most important ground-water reservoir in the province. From this reservoir many thousands of wells dug to depths ranging from a few feet to 100 feet derive individual sustained yields of 5,000 to 25,000 gallons per day, averaging about 15,000 gallons per day. The water is generally hard but otherwise of good quality. The content of dissolved solids is generally less than 1,000 parts per million.

Cenozoic Sedimentary Province.—The Cenozoic sedimentary province comprises (1) three narrow coastal plains on the Malabar and Coromandel Coasts, (2) coastal fringes on the Kathiawar and Kutch peninsulas, (3) an extensive embayment in western India, and (4) a belt of strongly-folded rocks in eastern India (Fig. 1). These areas are all underlain by semiconsolidated conglomerates, sandstones, and shales ranging in age from Late Cretaceous to late Tertiary.

The shales throughout the province are generally impervious and yield little or no water to wells. On the other hand, the conglomerates and sandstones, where well sorted, poorly cemented, and relatively undisturbed by

folding or faulting, are moderately or even highly permeable. Where such rocks are present in the zone of saturation, they form aquifers that sustain moderate to large withdrawals from wells. In the plains of the Malabar and Coromandel Coasts, seaward-dipping Miocene and Pliocene strata contain several water-bearing sandstones and conglomerates at depths ranging from 50 to 500 feet below the land surface. Drilled wells tapping these beds yield 10 to 500 gallons per minute, the individual yields depending on such factors as the well diameter, the screen length, and the number and thickness of aquifers penetrated. The water is commonly confined under artesian pressure. Where situated near the coast, wells that tap these aquifers commonly flow. For example, on the Coromandel Coast there are 150 or more wells that flow at rates of 50 to 500 gallons a minute. The water is low in dissolved solids but contains considerable iron and hydrogen sulfide. Similarly, wells 200 to 400 feet deep on barrier beaches of the Malabar Coast commonly flow at rates of 10 to 50 gallons per minute.

In the coastal fringes of the Kathiawar and Kutch peninsulas (Fig. 1), where the Miocene and Pliocene sandstones and conglomerates are slightly cemented and poorly sorted, they form aquifers of relatively low productivity. Wells dug in these rocks to depths of 25 to 75 feet commonly have individual yields averaging about 15,000 gallons per day. The water is generally brackish or even salty, the dissolved solids content ranging from 2,000 to more than 5,000 parts per million. In parts of the Tertiary embayment of western India, where the sandstones and conglomerates are unconsolidated and fairly well sorted, they form productive aquifers in the zone of saturation. For example, in Gujerat there are two or more soft sandstone aquifers at depths between 200 and 700 feet below the land surface that are intercalated with clay shales. Since 1950 about 500 irrigation wells have been drilled to tap these aquifers. Several tens of these wells in western Gujerat have artesian heads of 5 to about 25 feet above the land surface and flow at rates of 50 to 250 gallons per minute. Most of the other wells, which do not flow, yield 200 to 500 gallons per minute when pumped. The water has a dissolved-solids content of about 1,000 to 2,500 parts per million. In the northern part of the embayment near Bikaner, soft sandstones and conglomerates of probable Eocene age are trapped by dug and bored wells at depths of 325 to 450 feet below the land surface. The individual sustained drafts from these wells range from about 25 to 250 gallons per minute. The dissolved-solids content of the water is generally 1,000 to 2,000 parts per million.

The folded sandstones of Tertiary age in eastern India (Fig. 1) generally are poorly sorted and have lost much of their original permeability by cementation. They are not extensively developed by wells for water supplies, but they give rise to numerous springs of moderate flow in the hilly tracts of the Indo-Burmese frontier. The water is generally of good quality.

Cenozoic Fault Basins.—This province comprises three discrete fault basins—the Narmada, the Purna, and the Tapti Valleys (Fig. 1), each of which contains an extensive fill of unconsolidated Quaternary alluvium. The Narmada alluvial fill apparently lies in a rift valley or graben, but the Purna

and Tapti fills occur in assymetric basins formed by simple tilted fault blocks. In each of these valleys, water occurs principally in lenses of sand and gravel intercalated with silt and clay of the alluvium.

Recent exploratory drilling in the Narmada Valley has shown that the alluvium ranges in thickness from a few tens of feet to as much as 500 feet, and that it is highly variable from place to place in texture and sorting. Relatively impermeable clay and silt constitutes considerably more than half the bulk of the alluvium in a large part of the valley. However, in a number of areas, lenses of well-sorted water-bearing sand and gravel, a few feet to a few scores of feet thick, are intercalated with clay and silt. These sand and gravel lenses form aquifers, which can yield 300 to 600 gallons per minute to individual wells. The dissolved-solids content of the water generally ranges from about 100 to 500 parts per million.

The thickness of the alluvium in the Purna Valley is yet to be determined by deep exploratory drilling. However, the evidence of existing shallow wells and the geology of the valley indicate that the alluvium ranges from a feather-edge on the south side of the valley to a probable maximum thickness of 500 feet or more near the north side. The alluvium is predominantly fine-textured sand, silt, and clay in the central and southern parts of the valley, but in the northern part these materials are intertongued with lenses of coarse sand and gravel, which are generally saturated and form moderately productive aquifers. The ground water in the central and southern parts of the Purna Valley is commonly salty and unfit for many purposes, but in the northern part the water is of good quality and generally contains less than 500 parts per million of total solids.

The alluvial fill of the Tapti valley is less than 250 feet thick at most places and is deeply dissected by the Tapti River and its tributaries along the southern side of the valley. There are, however, several score irrigation wells of combined dug and bored construction that tap water-bearing sands and gravels intercalated with silts and clays in the Tapti alluvium. These wells generally range in depth from 100 to 200 feet and yield 100 to 250 gallons per minute. The water generally contains less than 500 parts per million of dissolved solids.

Ganges-Brahmaputra Alluvial Province.—The Ganges-Brahmaputra alluvial province comprises the Ganges Plains, the contiguous Brahmaputra valley, and the deltaic plains of the Ganges and Brahmaputra Rivers (Fig. 1). Most of this lowland is in the great crustal downbuckle, or foredeep, between the Himalayan orogen and the Peninsular shield. The foredeep is filled with late Tertiary and Quaternary alluvium which in places attains a thickness of 2,000 feet or more. This alluvial fill constitutes a vast ground-water reservoir, which is, or potentially is, the most productive in India. Many tens of thousands of small water supplies for domestic, stock, and village use and small-scale irrigation and several thousand large supplies for irrigation projects, for public water supplies, and for industrial use are obtained from water-bearing sands and gravels of the Ganges-Brahmaputra alluvium.

The ground water occurs in three distinct physiographic and hydrologic

belts, the "bhabbar," the "terai," and the "axial." The "bhabbar" comprises the higher parts of the compound alluvial fans of streams issuing from the Himalayan highland and forms a belt some 6 to 8 miles wide along the foot slopes of the Himalayan front. The alluvium of the bhabbar is composed largely of bouldery to pebbly gravel and coarse sand. Ground water in these deposits is generally unconfined. Along the mountain margin of the bhabbar the water table is commonly as much as 100 feet or more below the land surface, but downslope the depth to water progressively decreases to a line of springs where the water table intersects the land surface. This spring line marks the mountainward limit of the "terai." The "terai" is a belt some 5 to 10 miles wide parallel to the bhabbar, and comprises the lower parts of the alluvial fans. The alluvium of the terai belt is made up of tongues of permeable water-bearing gravel and sand intercalated with relatively impermeable silt and silty clay. Water in strata at depths of less than 100 feet in the terai is generally unconfined, and the water table is ordinarily within 10 feet of the land surface. However, water in the aquifers deeper than 100 feet is generally confined, and wells that tap them at depths greater than 200 feet commonly flow at the land surface. The lower slopes of the terai merge imperceptibly with the "axial" belt, which comprises the bulk of the alluvium laid by the larger streams of the Ganges and Brahmaputra systems. The alluvium of the axial belt is composed of intercalated lenses of relatively impervious silt and clay, and pervious, well-sorted medium to fine-grained sand and some fine gravel. The lenses of sand and gravel in the axial alluvium are water bearing at depths ranging from near the land surface down to a depth of 1,500 feet at Lucknow (Fig. 1). Ground water in the shallow aquifers is unconfined, and the water table is commonly 15 to 40 feet below land surface. Water in the deeper aquifers is confined or partially confined, but the hydrostatic head is not greatly different in altitude from the water table. The water in the Ganges-Brahmaputra alluvium is commonly hard but generally contains less than 500 parts per million of dissolved solids. In some localities, however, particularly near the margins of the Peninsular plateau, the ground water is brackish or even salty.

Since 1933 several thousand drilled irrigation wells 10 to 16 inches in diameter have been constructed by Indian government agencies in the Ganges Plains west of longitude 85°. Most of the wells are screened in water-bearing sands between 150 and 500 feet below the land surface. The draft from individual wells is generally from about 300 to 800 gallons per minute.

Himalayan Highland Province.—The Himalayan highland comprises a complex of rocks, largely sedimentary, ranging in age from Paleozoic to Cenozoic. These rocks include limestone, sandstone, shale or their metamorphic equivalents and some intrusives, which are chiefly granite. Most of these rocks have been greatly deformed by thrust faulting and folding in the orogeny of the Himalayas. The highland is traversed by deep gorges and narrow valleys, some of which are partly filled with Quaternary alluvium.

The consolidated rocks give rise to numerous small but perennial springs which are the chief source of domestic, stock, and village water supplies in

the region. However, in the lower reaches of the larger valleys many dug wells used for domestic and stock purposes, for irrigation, and for public supplies tap beds of coarse-grained gravel and sand in the alluvium at depths generally less than 100 feet. The alluvial fills of the Himalayan valleys also constitute important underflow conduits which transmit large quantities of water to the ground-water reservoir of the Ganges-Brahmaputra alluvial province. In most places the ground water of the Himalayan province is soft and contains less than 500 parts per million of dissolved solids.

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SOME MINERALOGICAL RELATIONSHIPS IN THE SYSTEM Fe_2O_3–Fe_3O_4 AND THE COMPOSITION OF TITANOMAGHEMITE

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ABSTRACT

Chemical, mineragraphic and X-ray investigations are carried out on minerals belonging to the system Fe_2O_3–Fe_3O_4. The existence of minerals intermediate in composition between magnetite and maghemite is proved with certainty and a brief discussion is given on the oxidation of natural magnetite. Similar data are presented on titanomaghemites and an attempt is made to explain the great variations in their chemical composition. It is suggested that titanomaghemites are formed mainly by the oxidation of titanomagnetite Fe_3O_4–γ–$FeTiO_3$ and that they represent a series varying in composition from γ–Fe_2O_3.Fe_3O_4 – γ–$FeTiO_3$ to γ–Fe_2O_3–TiO_2.

INTRODUCTION

THE fact that there are two polymorphic types of Fe_2O_3, 1) rhombohedral α–Fe_2O_3 (hematite), and 2) cubic γ–Fe_2O_3 (maghemite) makes it convenient to treat the discussion of the mineral phases in the system Fe_2O_3–Fe_3O_4 in two sections: I. α–Fe_2O_3–Fe_3O_4 and II. γ–Fe_2O_3–Fe_3O_4. Of these two sections, the system α–Fe_2O_3–Fe_3O_4 is better known as much work has been done on both its natural minerals and its synthetic preparations; of special importance is the thorough work by Greig and his co-workers (14). On the other hand, the system γ–Fe_2O_3–Fe_3O_4 is practically only known in the artificial preparations (16) and is, therefore, the main object of this paper especially as regard to natural minerals, while the system α–Fe_2O_3–Fe_3O_4 will be dealt with rather summarily.

Maghemite has been reported and described from various localities by Sosman and Posnjak (33), Wagner (40), Walker (42), Nieland (26), Ödman (27), Newhouse and Glass (24), Frankel and Grainger (11) and Schwellnus and Willemse (32), and many chemical analyses were given. However, most of the materials studied were not homogeneous, and, as far as the author is aware, no X-ray data were presented with the exception of the work by Newhouse and Glass. The measured lattice parameters given by Newhouse and Glass (24, p. 703) are certainly not precise and they did not attempt to explain the considerable variations in the values obtained for their different specimens (ranging from a = 8.30 Å to a = 8.369 Å).

Most of the "maghemites" described in the literature, especially those from the Bushveld Complex, are in fact certain types of titanomaghemite, a name originally given by the present author (2, p. 71) for maghemites with an appreciable content of TiO_2. In the present work, the term maghemite is restricted, as originally intended by Wagner (40), to natural γ–Fe_2O_3 and

not to γ-$(Fe,Ti)_2O_3$ as suggested by Walker (42). The term "oxymagnite," an abbreviation of oxidized magnetite, used by Winchell (46, 47) for maghemites is unacceptable owing to the fact that natural γ-Fe_2O_3 may be formed not only by the oxidation of magnetite but also by the dehydration of lepidocrocite. The interpretation of the variation in composition of titanomaghemites, which are proved to be related to the system γ-Fe_2O_3-Fe_3O_4, is given in section III of this paper.

The present study embraces the results of a combined chemical, mineragraphic, and X-ray investigations on a large collection of specimens from various localities. X-ray powder photographs were used to determine the homogeneity of the materials analyzed, to identify the mineral phases present and to determine the relationship between the composition and the unit-cell dimensions. The X-ray powder photographs were taken with filtered cobalt radiation ($k\alpha_1$ = 1.78890 Å, $k\alpha_2$ = 1.79279 Å, $k\alpha$ = 1.7902 Å), using a Philips diffraction apparatus (type 11704), and a 114.59 mm diameter camera. The film was mounted according to the Straumanis method (3).

TABLE 1

EFFECT OF TEMPERATURE ON THE EXTENT OF SOLID SOLUTION OF α-Fe_2O_3 IN Fe_3O_4 (DATA TAKEN FROM GREIG ET AL., 14)

Temperature °C.	Composition of maximum solid solution	
	Fe_3O_4	α-Fe_2O_3
1,075	92	8
1,200	87	13
1,388	75.5	24.5
1,452	70	30

Seven new chemical analyses of pure carefully separated materials, the homogeneity of which was determined by powder photographs, were made. To avoid iron or steel contamination, the ores were crushed between two horizontal discs of Cu–Be alloy under a pressure of 3–4 tons/in², and not in a hardened steel mortar. Separation was carried out using an A.C. electromagnet, a permanent magnet, and further purification was attained by centrifuging in broform (2, p. 27–34).

I. THE SYSTEM α-Fe_2O_3-Fe_3O_4

(Magnetite-Hematite Solid Solutions)

The results of Greig and co-workers (14) indicate that the solubility of Fe_3O_4 in α-Fe_2O_3 is very small at all temperatures up to 1,450° C. (1 wt. % or less), whereas the solubility of α-Fe_2O_3 in Fe_3O_4 is small but noticeable at low temperatures and increases rapidly at high temperatures, reaching 30 wt. % at about 1,450° C as shown in Table 1.

By heating a specimen of partially martitized magnetite (containing about 5% hematite)—from Edison, New Jersey—in evacuated silica glass tubes at 1,050° C for 48 hours, complete homogenization resulted. X-ray powder photograph of the quenched charge, showed only magnetite lines; no change in the size of the unit cell occurred.

The systematic investigations of the system Fe_3O_4–α-Fe_2O_3 have all been

carried out at high temperatures, 1,100° C and above. By extrapolation of Greig's curve (14, p. 268), the solubility of Fe_2O_3 in Fe_3O_4, at ordinary temperatures, is almost negligible. However, such an extrapolation from 1,100° C down to ordinary temperatures is unreliable. Mason (21, p. 124–125), using data given by Hägg in his work on γ–Fe_2O_3 (16, p. 98), tried to draw the solubility curve at low temperatures. Hägg, by heating homogeneous samples of composition between Fe_3O_4 and γ–Fe_2O_3, in sealed tubes at 675° and 490° C, had decomposed them into α–Fe_2O_3 and a magnetite solid solution poorer in oxygen than the original homogeneous phase. The cell-edge of the magnetite phase thus formed was 8.377 A. From Hägg's curve (p. 97) showing the relation between the composition of Fe_3O_4–γ–Fe_2O_3 solid solutions and the cell-edge, the magnetite corresponded to the formula $FeO_{1.344}$. Mason (21) thought that as this would correspond to Fe_3O_4 with 7 wt.% Fe_2O_3 in solid solution, then, by extrapolation, magnetite can contain up to about 7 wt.% hematite at ordinary temperatures. However, his interpretation is erroneous, as the magnetite obtained by Hägg actually contained γ–Fe_2O_3, not α–Fe_2O_3, and consequently Mason's extrapolation curve (p. 122) cannot be accepted.

From the above remarks it is evident that at the temperatures of igneous rock formation the extent of solid solution of hematite in magnetite is very limited (definitely less than 8% Fe_2O_3), whereas hematite can take less than 0.5% Fe_3O_4 and must correspond almost exactly to the formula Fe_2O_3. Ramdohr (30, p. 739) observed in an inclusion in basalt from Bühl, near Kassel, granular well-defined hematite and magnetite occurring side-by-side in a typically recrystallized state, but without any sign of solid solution. The presence of excess Fe_2O_3 in the analyses of some magnetites is in most cases possibly due to maghemite, and not hematite in solid solution, as will be shown in the next section. Maghemite-magnetite solid solutions could possibly be distinguished from the hematite-magnetite solid solutions by the considerable decrease in the size of the unit cell of magnetite with the increase of γ–Fe_2O_3 in solid solution (Fig. 1). Greig and co-workers (14, p. 296–297), have found that in artificial preparations of Fe_3O_4 with 15% α–Fe_2O_3 in solid solution, the displacement of the lines was barely perceptible, and in those containing 22% α–Fe_2O_3 the decrease in the edge of the unit cell was not more than 0.01 A

Since temperatures of 1,100°–1,200° C and higher are necessary to increase the solubility of α–Fe_2O_3 in Fe_3O_4, so as to allow unmixing to take place on cooling, there is little possibility of finding oriented intergrowths of hematite in naturally formed magnetite. As far as the author is aware, only four examples of such an occurrence have been observed. Newhouse (23, p. 19) while describing the opaque minerals in 265 different igneous rocks, recorded what he considered to be ex-solved hematite in magnetite from a basalt from Mt. Etna. Edwards (10) described in a small pebble from Cairns, Queensland, Australia, and in grains from beach sands at Viti Levu, Fiji, intergrowths of hematite in the (111) directions of magnetite with 20 and 15 percent hematite, respectively. Another occurrence was recently noted by Baker (1) in amphibolite from Matapau, New Guinea. The pro-

portion of host magnetite to unmixed hematite lamellae in the intergrowth, measured micrometrically, is 88:12. Both Edwards and Barker have noticed that, according to Greig's data (Table 1), the ratio of the hematite intergrowths to the magnetite would indicate temperatures of about 1,200°–1,300° C, which are unduly high for igneous rocks. They predicted some additional unknown factor as causing the formation of solid solution in nature at temperatures lower than those found in the laboratory by Greig

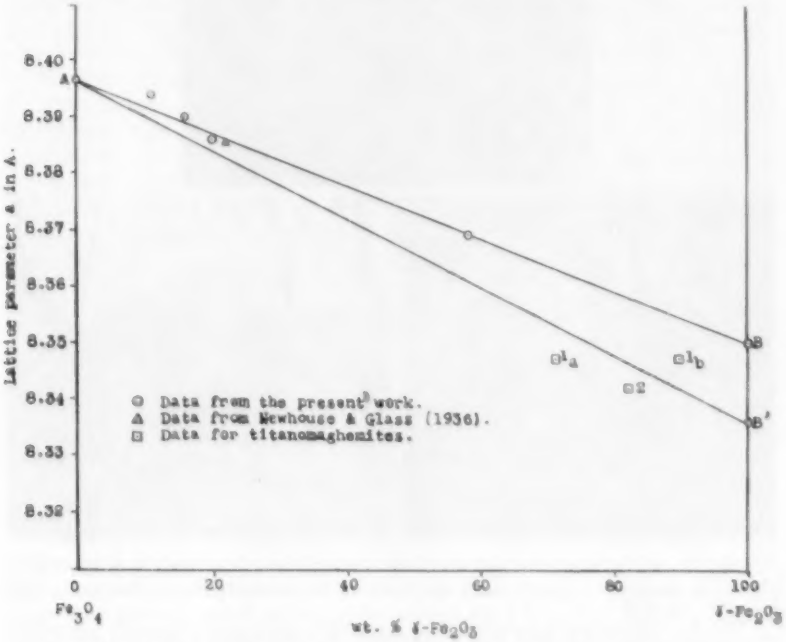

FIG. 1. Variation of lattice parameters with composition in the series γ-Fe_2O_3–Fe_3O_4. Parameters of γ-Fe_2O_3 are represented by B (using Haul and Schoon's (17) value) or B′ (using the mean of B and the value given by Hägg (16)).

and his associates. However, an X-ray examination of 2 samples of Fiji beach sands—sent to the writer by Professor Edwards—did not reveal more than 7 percent hematite, a result that agrees with Greig's data. Besides, from a study of the polished section of Baker's amphibolite from Matapau (Fig. 2), the author could not reject the possibility that some of the hematite measured by him is actually martite. It should be pointed out here that the ex-solution texture is practically identical with the texture resulting from the replacement of magnetite by hematite (martitization), which results from either hypogene or supergene oxidation of magnetite. The only distinction is that with the ex-solution intergrowths, the hematite lamellae

are of uniform width and are evenly distributed through the magnetite, whereas with oxidation, the alteration to hematite is most pronounced at the margins of the magnetite crystals or along cracks and the hematite lamellae produced vary considerably in width in different parts (Figs. 2, 3).

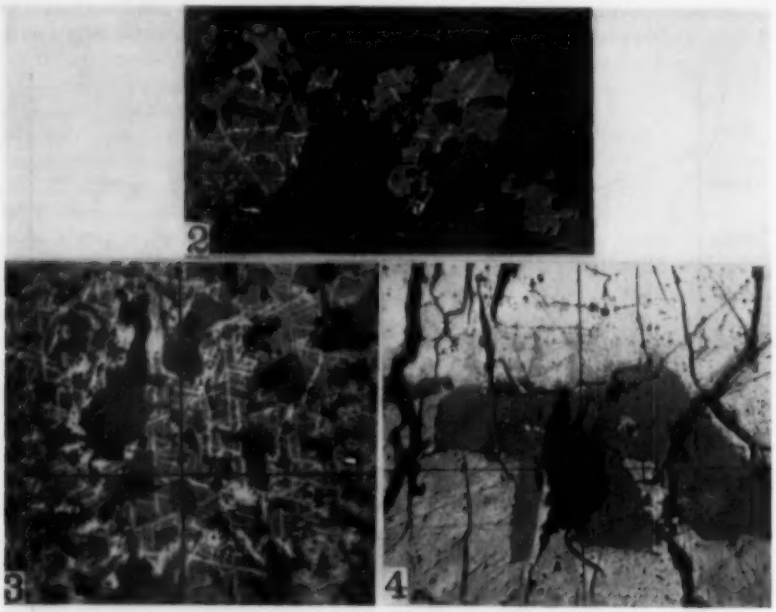

FIG. 2. Ex-solution intergrowths of hematite lamellae (white) in the (111) planes of magnetite (gray), in a specimen of amphibolite from Matapau, New Guinea. × 430.

FIG. 3. Martitized magnetite; the magnetite (dark gray) is partly altered to hematite (white). The hematite differs from that in Figure 1 in being concentrated at the margins and along the octahedral cleavage planes; the hematite lamellae may vary considerably in width in different parts. Schischimskaja, C. Kussa. Urals, U.S.S.R. × 525.

FIG. 4. Irregular grain of ilmenite (dark gray) in titanomaghemite (light gray), with limonite (black) along the cracks. Bon Accord, Bushveld Complex, Transvaal. × 110. Nicols partially crossed.

II. THE SYSTEM γ–Fe_2O_3–Fe_3O_4

(Maghemite–Magnetite Solid Solutions)

Before establishing the relationship between magnetite and maghemite it would be preferable to discuss the maghemite structure. Maghemite, similar to magnetite, has an inverse spinel structure but it differs in possessing a defect lattice; $\frac{1}{9}$ of the iron positions in the magnetite lattice are

vacant in γ–Fe_2O_3 (16, 37, 19). Thus the unit cell is not $Fe_{24}O_{36}$—as was previously suggested by Welo and Baudisch (43) and Twenhofel (36)—but $Fe_{21\frac{1}{3}}O_{32}$. However, Haul and Schoon (17) have observed a number of weak additional lines on the X-ray powder photographs at γ–Fe_2O_3, which they suggested indicate either a lower symmetery or a larger unit cell than has been postulated for this substance. A more possible explanation is that the vacant positions are regularly arranged in the lattice. Verwey (37) has shown that the vacant positions are probably from 6-fold co-ordination positions. Some of these additional lines, especially two lines with spacings 5.9 and 4.1 A appeared in the X-ray powder photographs of the maghemite-magnetite samples that were examined in the present work (Table 3).

Since Fe_3O_4 and γ–Fe_2O_3 have similar type of structure and the change from the former to the latter only involves a replacement of $3Fe^{2+}$ in 6-fold co-ordination by $2Fe^{3+}$, it would be expected that solid solution is complete between the two substances. Hägg (16, p. 98) showed that the oxidation of Fe_3O_4 to γ–Fe_2O_3 is a continuous process, the cell-edge decreasing continuously from 8.380 Å for Fe_3O_4 to 8.322 Å for γ–Fe_2O_3. It is therefore conceivable that all stages in the oxidation of magnetite to maghemite may take place, and consequently the optical and physical properties may also vary continuously from magnetite to maghemite.

All the analyses of "maghemite" which have been published show a certain percentage of FeO (Table 2). This FeO was usually considered as being combined with TiO_2 present, as ilmenite (especially in specimens from the Bushveld occurrences, Table 5), or as being present as remnants of magnetite. In the homogeneous non-titaniferous specimens, however, the FeO occurs in the γ–Fe_2O_3 structure which will thus represent a substance intermediate in composition between Fe_3O_4 and γ–Fe_2O_3. These intermediate substances have not been previously recognized, but in the present work their existence is proved with certainty.

Table 3 shows the results of X-ray measurements of such samples together with similar data for titanomaghemite and for synthetic γ–Fe_2O_3 for the purpose of comparison. The powder photographs showed only the magnetite pattern (with the exception of sample 6 from Co. Antrim, Ireland which showed two faint lines of ilmenite, which was also indicated in the analysis) and there was a distinct displacement of the lines. Hematite lines were absent and there was no indication of shadowing or doubling of the "magnetite" lines by another spinel of slightly different cell-dimensions (e.g., maghemite). Accurate measurements of the lattice parameters gave values ranging between 8.368 Å and 8.395 Å which are lower than those of magnetite (a = 8.3963 Å; Basta, 1957) but higher than the cell dimensions of maghemite (a = 8.322 Å; 16 to a = 8.350 Å; 17).

These four samples were chemically analyzed and the analyses were recalculated into possible spinel molecules, ilmenite and silicates following the method applied by Vincent and Phillips (38). The sequence of recalculation follows the order in which the molecules are arranged in Table 2, and shows that in all the four samples there remained, after recalculating the spinel molecules, an appreciable excess of Fe_2O_3 which ranged between about

TABLE 2

CHEMICAL ANALYSES OF MINERALS INTERMEDIATE IN COMPOSITION BETWEEN MAGNETITE AND MAGHEMITE, WITH A RECALCULATION INTO END-MEMBERS (IN ASCENDING ORDER WITH INCREASE IN THE PERCENTAGE OF THE MAGHEMITE MOLECULE IN THE NORM)

	1	2	3	4	5	6	7	8
FeO	27.93	26.08	22.90	24.48	15.30	12.75	8.67	2.40
MgO	0.14	0.18	1.88	0.10	0.30	0.91	traces	—
MnO	0.07	0.58	0.10	—	1.43	0.18	—	—
CaO	0.03*	traces	1.00	traces	0.43	0.76	traces	—
Fe_2O_3	69.88	70.46	69.88	75.26	73.75	80.63	89.15	85.30
Al_2O_3	0.34*	traces	0.16	traces	2.96	0.30	0.04	—
V_2O_3	0.02*	nil	0.18	—	0.31	0.12	—	—
Cr_2O_3	0.07*	nil	0.01	—	—	0.01	—	—
TiO_2	0.16	0.84	0.49	traces	0.35	2.54	1.37	—
SiO_2	1.07*	1.24	2.20	0.53	2.35	0.84	1.15	—
H_2O	n.d.	n.d.	n.d.	—	3.02	n.d.	—	3.10
Rem.	—	—	—	—	—	—	—	4.30
Total	99.71	99.38	98.79	100.37	100.19	99.03	100.38	95.10
Recalculated compositions (wt. %)								
$CaO.SiO_2$	0.07	—	2.32	—	0.93	1.57	—	—
$MgO.SiO_2$	0.35	0.45	1.66	0.25	0.75	0.05	—	—
$FeO.SiO_2$	1.83	2.12	—	0.86	3.10	—	2.51	—
$MgO.Al_2O_3$	—	—	0.23	—	—	0.43	—	—
$FeO.Al_2O_3$	0.52	—	—	—	5.05	—	0.07	—
$CaO.Fe_2O_3$	—	—	—	—	—	—	—	—
$MgO.Fe_2O_3$	—	—	1.56	—	—	3.82	—	—
$MnO.Fe_2O_3$	0.23	1.84	0.23	—	4.62	0.58	—	—
$FeO.V_2O_3$	0.04	—	0.27	—	0.44	0.22	—	—
$FeO.Cr_2O_3$	1.12	—	0.02	—	—	0.02	—	—
$FeO.TiO_2$	0.30	1.59	0.93	—	0.67	4.83	2.59	—
$FeO.Fe_2O_3$	85.27	77.89	72.15	77.38	35.68	33.47	19.50	7.73
$Fe_2O_3.H_2O$	—	—	—	—	20.80	—	—	22.47
γ–Fe_2O_3	10.95	15.87	18.78	21.88	28.09	54.12	75.67	61.58
Total	100.68	99.16	98.15	100.37	100.13	99.11	100.34	91.78
Recalculated wt. % of γ–Fe_2O_3 in magnetite molecule:	11.15	16.0	20.10	22.0	38.0	58.40	79.40	88.8

Analyses 1, 2, 3 and 6 are new analyses. Spectrographic determinations (*) in no. 1 by D. Calkin.

1. Maghemo-magnetite from an iron ore at Bovey Tracey, Devon, S. W. England. Analyst, H. B. Milner. S 172.
2. Maghemo-magnetite from a spotted ore at Mt. Blagodot, Urals, U.S.S.R. Analyst, W. H. Herdsman. S 391.
3. Maghemo-magnetite from Mourne, Co. Down, Ireland. Analyst, H. B. Milner. S 407.
4. Maghemo-magnetite from Windpass Mine, British Columbia. Analyst Keyes (Newhouse and Glass, 1936, p. 701).
5. Maghemo-magnetite from Bukusu Hill alkaline complex, Uganda. Analyst, H. J. Broughton (Broughton, Chadwick and Deans, 1950, p. 263).
6. Magneto-maghemite from basalt, Co. Antrim, Ireland. Analyst, H. B. Milner. S 456.
7. Maghemite and magnetite from Alameda Co., California. Analyst, Keyes (Newhouse and Glass, 1936, p. 701).
8. Maghemite from Iron Mountain, Shasta Co., California. Analyst, J. C. Hostetter (Sosman and Posnjak, 1925, p. 333).

11 percent (Table 2, Col. 1) to about 54 percent (Table 2, Col. 6). Table 2 also shows the weight percentage of this excess Fe_2O_3 recalculated after the subtraction of silicates, ilmenite and limonite (when present).

TABLE 3

X-RAY POWDER DATA FOR MINERALS OF MAGNETITE-MAGHEMITE SOLID SOLUTIONS AND FOR TITANOMAGHEMITE

CoK_α RADIATION, Fe FILTER, CAMERA DIAMETER 114.59 MM. SPACINGS ARE COMPARED WITH THOSE FROM THE A.S.T.M. INDEX CARD D 4-0760, RECOMMENDED BY THE JOINT COMMITTEE AS THE BEST DATA FOR γ-Fe_2O_3 (HAUL AND SCHOON, 1939).

I	1	2	3	6	S542	4-0760		hkl
	d(meas)	d(meas)	d(meas)	d(meas)	d(meas)	d(A)	I	
vvw			5.931	5.925	5.917	5.90	2	110
mw	4.837	4.835	4.833	4.824	4.807	4.82	5	111
vvw			4.145	4.142	4.115	4.18	1	200
vw				3.721*	3.712*	3.73	5	210
						3.41	2	211
s	2.965	2.961	2.961	2.957	2.949	2.95	34	220
vvw				2.737*	2.735*	2.78	19	300
vvs	2.527	2.526	2.524	2.522	2.515	2.52	100	311
vw	2.417	2.415	2.415		2.404	2.41	1	222
						2.32	6	320
vw					2.222*	2.23	.5	321
s	2.096	2.094	2.091	2.090	2.084	2.08	24	400
						1.87	.5	420
ms	1.712	1.710	1.711	1.707	1.703	1.70	12	422
vs	1.614	1.613	1.611	1.608	1.605	1.61	33	{511, 333}
						1.55	.5	{432, 520}
						1.53	1	521
vs	1.482	1.482	1.480	1.478	1.474	1.48	53	440
						1.43	1	{433, 530}
vw	1.325		1.324	1.321	1.320	1.32	7	620
w	1.279	1.278	1.277	1.275	1.272	1.27	11	533
						1.26	3	622
w	1.210		1.209	1.207	1.204	1.21	5	444
w	1.1209		1.1199	1.1182	1.1148	1.12	7	642
ms	1.0919	1.0919	1.0902	1.0892	1.0862	1.09	19	{553, 731}
						1.07	1	650
mw	1.0486	1.0483α_1	1.0476α_1	1.0457	1.0423	1.04	8	800
						1.03	1	{741, 811}
vvw	0.9887	0.9885	0.9879	0.9854	0.9829			{660, 822}
mw	0.9689α_1	0.9687α_1	0.9680α_1	0.9660α_1	0.9638α_1			{555, 751}
w	0.9689α_2	0.9687α_2	0.9680α_2	0.9660α_2	0.9638α_2			
w	0.9384α_1	0.9382α_1	0.9374α_1	0.9356α_1	0.9332α_1			840
vw	0.9384α_2	0.9382α_2	0.9375α_2	0.9358α_2	0.9332α_2			840

1. Maghemomagnetite, Bovey Tracey, Devon; a = 8.394 ± 0.001 A.
2. Maghemomagnetite, Mt. Blagodot, Urals; a = 8.390 ± 0.001 Å.
3. Maghemomagnetite, Mourne, Co. Down, Ireland; a = 8.386 ± 0.001 Å.
6. Magnetomaghemite, Co. Antrim, Ireland; a = 8.369 ± 0.001 Å.
S542. Titanomaghemite, Bon Accord, Transvaal; a = 8.3475 ± 0.001 Å.
4-0760. Artificial γ-$Fe_2{}''O_3$ (Haul and Schoon, 1939); a = 8.350 Å.
* Ilmenite lines.

Under the microscope, the minerals appear homogeneous with the highest magnification (except for few ilmenite lamellae in sample 6), gray with a slightly bluish tint, isotropic, and of moderate reflectivity; no hematite was observed.

The previous characters in polished sections together with the fact that the X-ray powder photographs did not show any hematite lines nor any doubling or shadowing of the spinel pattern proves for certainty that these samples are not a mixture of magnetite with any form of Fe_2O_3 and that the excess Fe_2O_3, observed in the recalculated analyses, must be present in solid solution in the magnetite lattice. That this excess Fe_2O_3 may reach up to 58 percent suggests that it is in the form of γ–Fe_2O_3. This is in complete conformity with the X-ray measurements as it was possible to follow the decrease in the size of the unit cell of magnetite with the progressive increase in its maghemite content (Table 3).

Figure 1 shows the relationship between the cell-edge and composition of the magnetite–maghemite solid solutions. The composition of the solid solutions is taken as the weight percentage of γ–Fe_2O_3 and Fe_3O_4 calculated after addition of all the other spinels [1] ($MgO.Al_2O_3$, $FeO.Al_2O_3$, $CaO.Fe_2O_3$, $MgO.Fe_2O_3$, $MnO.Fe_2O_3$, $FeO.V_2O_3$, and $FeO.Cr_2O_3$) to magnetite followed by subtraction of silicates and ilmenite and rounding off to 100 percent (see Table 2). A straight line (AB) has been drawn between 8.396 Å the cell-edge of magnetite (3) and 8.350 Å the value given by Haul and Schoon (17) and recommended by the Joint Committee of the A.S.T.M. Index Cards (1954) as the best data for γ–Fe_2O_3. The value 8.322 Å determined by Hägg (16), and usually quoted in the literature, is certainly unduely low as it may be noted that his value for magnetite (8.380 Å) is also much lower than the present well-accepted value of 8.396 Å. Point B′ corresponds to a = 8.336 Å [2] which is the mean of the values given by Hägg and that of Haul and Schoon for γ–Fe_2O_3. The present determinations of the lattice parameters of natural magnetite-maghemite solid solutions fall fairly close to the line AB, indicating agreement with Vegard's mixture law, though a less satisfactory fit is obtained if line AB′ is used. However, it must be noted that precise correlation between cell-dimensions and compositions of the samples is hardly to be expected since the exact manner of distribution of ions other than Fe^{2+} and Fe^{3+} in the lattice cannot be determined and the calculated mineral compositions are somewhat arbitary.

Newhouse and Glass (24, p. 701) gave the chemical analysis of a specimen of magnetite from Windpass mine, British Columbia, which was almost free of oxides other than those of iron (Table 2, Col. 4). On recalculation of the analysis, an excess of about 22% Fe_2O_3, over that which is necessary for the formation of magnetite, appeared. In spite of the fact that their X-ray powder photograph did not show any maghemite pattern, and that the cell-edge was 8.369 Å, which is lower than that for pure magnetite, they errone-

[1] The only foreign ion of appreciable amount is that of Mg which, however, corresponds to not more than 3.8% $MgO.Fe_2O_3$ (Table 2, Col. 6) and will have very little effect on the cell dimensions of magnetite as will be discussed later.

[2] A similar value of a = 8.335 Å was given by Gaglioti and D'Agostino (1936) also for γ–Fe_2O_3.

ously considered it to be a heterogeneous mixture of magnetite and maghemite. It may be noted that all the values of lattice parameters given by Newhouse and Glass are much lower than the more accurate values determined recently for the same specimens,[3] as could be seen from the accompanying table:

Specimen	a in Å by Newhouse and Glass	a in Å by other authors
1) Magnetite, Mineville, N. Y.	8.379	8.392 ± 0.001 (Schmidt and Vermaas, 1955)
2) Magneso-titanomagnetite, Magnet Cove, Arkansas	8.371	8.396 ± 0.001 (Basta, 1957)
3) Titanomaghemite, Bon Accord, Transvaal (Walker's specimen)	8.319	8.342 ± 0.001 (Basta, this paper)

On calibration of the original value given by Newhouse and Glass for the Windpass specimen, the approximate figure of 8.386 Å was obtained for its lattice parameter. When this value was plotted against the recalculated composition (Table 2, Col. 4), the point obtained falls in between the two lines AB and AB′ and fairly close to both, indicating that this specimen is undoubtedly another case of magnetite containing maghemite in solid solution.

It is possible that the occurrence of homogeneous minerals intermediate in composition between magnetite and maghemite, and which may represent stages in the oxidation of magnetite, are not uncommon. This possibility would account for some of the contradictory statements on the optical characters of magnetite in polished sections and may explain some of the considerable differences in its physical data reported in the literature. The author suggests the two terms "maghemomagnetite" and "magnetomaghemite" to indicate homogeneous magnetite containing less than 50% γ-Fe_2O_3 and more than 50% γ-Fe_2O_3, respectively, in its lattice structure. The term maghemite should be restricted, as already stated before, to natural substances of composition almost exactly γ-Fe_2O_3, and with cell dimensions ranging between 8.30 and 8.35 Å. Accurate identification can only be attained when the carefully separated minerals have been chemically analyzed in detail and precise measurement of the lattice parameters obtained, in addition to careful examination with the microscope. On going through the literature, the author was able to ascertain the identification of maghemite in the true sense, i.e., natural γ-Fe_2O_3 only in two occurrences: from Alameda Co., California (24) and from Iron Mountain, Shasta Co., California (33). The recalculated compositions, although showing a certain percentage of Fe_3O_4 (Table 2, Cols. 7, 8), yet the lattice parameters as given by Newhouse and Glass (8.326 and 8.30 Å, respectively) are too low to indicate that this Fe_3O_4 is in solid solution.

On the other hand, many of the magnetite samples examined by the author, gave a somewhat lower value of the cell-edge than that of pure

[3] The measurements given by Newhouse and Glass are mostly averaged data and the wave length values assumed for their Co k_α radiation used, differ appreciably from the present values.

Fe_3O_4, which may be due to partial oxidation to maghemite. Such possible maghemomagnetites are from the following occurrences: East of Cload Bay, in dolerite; Coverack, Lizard, England, in troctolite; near Damascus, Syria, in basalt; Disho Island, Greenland, in basalt; Berggiesshübel, Saxony; Schmiedeberg, Silesia, at Lake Shirwa, East Africa and Schischimskaja, Urals. The X-ray measurements should be supplemented by detailed chemical analysis as the cell-edge of magnetite can also be lowered by other elements replacing iron (2, p. 437–438). However, most replacements in magnetite, by manganese and titanium, result in an increase in the lattice parameters, and other substitutions by Mg^{2+}, Co^{2+}, Ni^{2+}, Al^{3+} and Cr^{3+} are

TABLE 4

CHEMICAL ANALYSES AND CELL-DIMENSIONS OF SOME HIGHLY SUBSTITUTED MAGNETITES

	1	2	3		1′	2′	3′
FeO	28.40	21.83	26.58	$CaO.SiO_2$	—	0.73	0.23
MgO	1.85	7.18	5.83	$MgO.SiO_2$	2.58	—	0.02
MnO	0.06	1.82	n.d.	$MgO.Al_2O_3$	0.18	4.98	20.56
CaO	nil*	0.94	0.11	$FeO.Al_2O_3$	—	—	0.69
Fe_2O_3	67.57	57.11	46.95	$CaO.Fe_2O_3$	—	2.27	—
Al_2O_3	0.14*	3.62	15.14**	$MgO.Fe_2O_3$	3.76	28.60	—
V_2O_3	nil*	0.10	n.d.	$MnO.Fe_2O_3$	0.21	5.96	—
Cr_2O_3	nil*	0.01	n.d.	$FeO.V_2O_3$	—	0.16	—
TiO_2	0.05	6.98	5.01	$FeO.Fe_2O_3$	91.39	41.29	68.08
SiO_2	1.55*	0.38	0.13	$FeO.TiO_2$	0.09	7.59	8.12
				$2FeO.TiO_2$	—	8.39	2.06
Total	99.62	99.97	99.75	γ–Fe_2O_3	1.39	—	—
				Total	99.60	99.97	99.76

1. Magnesomagnetite from Kropferberg, Saxony, Germany. Analyst, H. B. Milner (new analysis—S 448). a = 8.3955 ± 0.001 Å.

2. Magneso-titanomagnetite from Magnet Cove, Arkansas, U.S.A. Analyst, H. B. Milner (new analysis—S 574). a = 8.3960 ± 0.001 Å.

3. Magneso-titanomagnetite from Magnet Cove, Arkansas, U.S.A. Analyst, Keyes (Newhouse and Glass, 1936, p. 701–703). a = 8.388 Å.

1′, 2′, 3′ are the wt. percentages of the end-members calculated from the analyses 1, 2, and 3.

* These constituents were determined spectrographically.

** The abnormally high value of Al_2O_3 is more likely due to a mistake in determining the analysis as the sum of Fe_2O_3 and Al_2O_3 is about the same as in analysis 2, and all the other constituents are comparable.

generally too low to influence the cell-edge values significantly. Exceptionally up to 8% MgO and up to 7% Al_2O_3 have been recorded in the analyses of magnetite, but such values are rare. Table 4 gives two new chemical analyses of such highly substituted magnetites. Analysis 1 of a magnetite from Kropferberg, Saxony contains about 2% MgO corresponding to 4% $MgO.Fe_2O_3$; the cell-edge, however, was 8.395 Å almost the same as pure magnetite. Analysis 2 of a titanomagnetite from Magnet Cove, Arkansas, showed in the recalculated composition about 28.6% $MgO.Fe_2O_3$ and about 5% $MgO.Al_2O_3$. The X-ray powder photograph however, also showed ordinary magnetite pattern with no change in the cell dimensions (a = 8.396 Å). It is possible that the presence of $2FeO.TiO_2$ (about 8%) and $MnO.Fe_2O_3$ (about 6%) which have cell dimensions 8.50 Å and 8.51 Å,

respectively (higher than of magnetite) has counteracted the decrease that would occur in the values of lattice parameters of magnetite due to the presence of $MgO.Fe_2O_3$ (a = 8.370 Å) and $MgO.Al_2O_3$ (a = 8.086 Å).

The Oxidation of Natural Magnetite

Whether natural magnetite is oxidized by heating to γ–Fe_2O_3—similar to the case of synthetic magnetite—or directly to α–Fe_2O_3 has been a matter of controversy for sometime and has been discussed by Sosman and Posnjak (33), Welo and Baudisch (43, 44), Gruner (15), Wagner (40), Twenhofel (36) and Starke (34).

Gheith (13) studied the oxidation of both synthetic and natural magnetite by differential thermal analysis. He stated that synthetic magnetite showed two exothermic peaks indicating its oxidation first to γ–Fe_2O_3 which in turn transforms to hematite, while natural magnetite that showed a single flat exothermic "plateau" is oxidized directly to hematite. However, the thermal curves of fine-grained natural specimens showed a small exothermic peak at 380–395° C. In spite of the fact that this small exothermic peak corresponds to a certain extent with the exothermic peak for the oxidation to γ–Fe_2O_3 of the synthetic specimens, yet he directly eliminated the possibility of the oxidation of this fine-grained natural magnetite to γ–Fe_2O_3. No chemical analysis or X-ray examination were carried out on the material produced after the first peak to prove whether it contained γ–Fe_2O_3 or not, and no explanation is given of the slight change in color (being more blue) of the samples. Gheith (13, p. 692–693) ascribed this first exothermic peak to the recrystallization of the extremely fine magnetite particles present in his samples, due to the high force of crystallization of magnetite.

Schmidt and Vermaas (31) carried out a number of differential thermal analysis experiments on natural magnetite. Their thermal curves showed two distinct exothermic peaks (360°–375° C and 580° C), the earlier of which was most pronounced in fine specimens and was attributed to surface oxidation to hematite (and not to recrystallization). However, they agreed with Gheith in their statement that no γ–Fe_2O_3 was detected at any stage.

The above interpretation given by Gheith (13) and by Schmidt and Vermaas (31) that natural magnetite is oxidized directly to hematite with no intermediate formation of γ–Fe_2O_3 is not in accordance with the results obtained in the present work as to the existence in nature of minerals intermediate in composition between Fe_3O_4 and γ–Fe_2O_3. These intermediate substances (Table 3, Fig. 1) represent stages in the oxidation of magnetite to maghemite and suggest the possibility that the first exothermic peak in the DTA curves for natural magnetite may represent partial oxidation to γ–Fe_2O_3.

This conclusion is supported by the most recent study conducted by Lepp (20) who heated finely ground magnetite from Mineville, N. Y., to 430° C and 500° C in a differential thermal analysis unit. X-ray powder photographs of the products showed strong magnetite patterns with few of the strongest hematite lines. Chemical analysis however, revealed a much higher content of Fe_2O_3 than could be explained by the few weak hematite

lines shown in the X-ray photographs. He concluded therefore, that most of the oxidation below 500° C must have involved a change to γ–Fe_2O_3, a conclusion that is supported by the broadening of the magnetite lines, of the heat-treated specimens, at high angle θ.

It may be noted here that the cell-edge of pure γ–Fe_2O_3 (a = 8.335 Å) is appreciably different from that of Fe_3O_4 (a = 8.396 Å) and it is therefore more conceivable that doubling of lines will appear at high angle θ. The fact that such doubling was not observed by Schmidt and Vermaas (31) nor by Lepp (20) who only observed that line broadening may be due to the possibility that the products of oxidation after the first exothermic peak, in case of natural magnetite, are Fe_3O_4 and γ–Fe_2O_3.Fe_3O_4 solid solutions and not a mixture of Fe_3O_4 and pure γ–Fe_2O_3 as Lepp thought. The second exothermic peak therefore, represents two processes: 1) the change of γ–Fe_2O_3.Fe_3O_4 solid solutions into α–Fe_2O_3, and 2) the direct oxidation of the remaining magnetite in the interior of the grains to hematite at temperatures higher than 550° C. This may account for some of the disagreements as to the temperature of inversion of γ–Fe_2O_3 into α–Fe_2O_3, and may explain the observation reported by Schmidt and Vermaas (31) that the second exothermic peak tends to split into two peaks in samples coarser than 325 mesh. If the particle size is extremely fine, most of the sample is oxidized to γ–Fe_2O_3 below 550° and very little or no magnetite is left, and consequently no splitting of the second exothermic peak appears.

From the work carried out by Hägg (16) and from the present study on natural minerals, it is evident that the oxidation of magnetite to maghemite is a continuous process (iron atoms being continuously removed from the magnetite lattice) and is therefore, different from the oxidation of magnetite to hematite which must be discontinuous. All the X-ray powder photographs of the samples examined in the present work showed the pattern of either magnetite or maghemite (or their solid solutions) but not a mixture of the two. The oxidation of magnetite to maghemite is generally independent of the crystallographic directions of magnetite in contrast to the oxidation of magnetite to hematite—the so-called martitization process.

The conditions governing whether magnetite will be oxidized to maghemite or hematite are not well known. The instability of maghemite at moderate temperatures suggests that oxidation of magnetite at temperatures above 400° C will result in hematite rather than maghemite. Thus it is hardly possible for maghemite to occur as an original mineral in medium to high-temperature deposits, and certainly not in metamorphic rocks. However, the oxidation of natural magnetite and the temperature of inversion of the maghemite thus formed are highly influenced by the presence of foreign atoms substituting Fe^{2+} or Fe^{3+} atoms in the original magnetite. Thus Michel (22) found that γ–Fe_2O_3 can be heated to temperatures above 700° C without inverting to the α-form, if it is stabilized by small amounts of MgO, BeO, NaOH and KOH, and Pouillard (28) has shown that in Al-bearing maghemites the temperature of inversion rises from 200–300° C for pure γ–Fe_2O_3 to 650° C when 7 percent of the Fe^{3+} is replaced by Al^{3+}. Examples of natural maghemomagnetites and magnetomaghemites showing

appreciable contents of Al^{3+}, Mg^{2+} and Mn^{2+} in their structure are given in Table 2 (up to 3% Al_2O_3, corresponding to a replacement of 5% Fe^{3+} ions by Al^{3+}). Rapid cooling of the order of 250° C may also be necessary for the preservation of the γ–Fe_2O_3.Fe_3O_4 solid solutions. Oxidation of magnetite to maghemite has been reported in some lavas, e.g., from Mt. Elgon, British East Africa (27) and from West Greenland (26). A new occurrence is recorded in the present paper, in a basalt from County Antrim, Ireland (its chemical analysis is given in Table 2, Col. 6). There is some indication that these previous examples were formed by hydrothermal solutions at relatively low temperatures and pressures, and not by strong atmospheric weathering.

III. TITANOMAGHEMITES

Many analyses of maghemite, especially of specimens from Bushveld occurrences, show a considerable amount of TiO_2 (Table 5) as has previously been reported by Wagner (41), Walker (42), Frankel and Grainger (11) and Schwellnus and Willemse (32). Different assumptions have been made to account for the form in which TiO_2 is present. Walker (42, p. 18), suggested that in lodestone from Bon Accord, Transvaal (also in the Bushveld Complex), all the titanium is probably present as Ti_2O_3, in solid solution in Fe_2O_3 and proposed the formula $(Fe, Ti)_2O_3$ for maghemite (Table 5, Col. 2). He was apparently supported in this belief by Professor Thomson's examination of a polished section of his material, which revealed "that 95 percent of the opaque material, apart from limonite, was made up of a single, definitely anisotropic mineral." However, Mason (21, p. 112) examined polished sections of specimens from the same locality, and found that the mass of the specimen consisted of an isotropic mineral—maghemite—in which irregular grains and minute oriented lamellae of ilmenite occurred, so small that they might have been easily overlooked by Professor Thomson. Mason thought that the amount of ilmenite in the polished sections could have accounted for the TiO_2 in Walker's analysis.

A sample from Walker's specimen (Royal Ontario Museum, No. 17382) was kindly sent to me by Professor W. H. Newhouse of Chicago University, having previously been supplied to him by Walker himself. An X-ray powder photograph of this specimen was taken which showed "maghemite" with a cell-edge of 8.342 ± 0.001 Å, together with weak, but definite, ilmenite reflections. By comparison with X-ray photographs of standard mixtures, the amount of admixed ilmenite was found to be about 4 percent, which is too low to account for all the TiO_2 (15.5%) present in the analysis, and thus Mason's previous statement cannot be accepted. Newhouse and Glass (24, p. 703), who had an X-ray analysis made by N. W. Buerger on the same specimen, could not observe ilmenite lines on their films, and gave the averaged value of 8.319 Å for the lattice parameter. Two other specimens (S 542, 536), also from Bon Accord, Transvaal, were examined by X-ray photographs and were found to give almost exactly the same pattern, with about 5 and 6 percent ilmenite, respectively. The X-ray measurements of S 542 are given in Table 3; the cell-edge is 8.3475 ± 0.001 A.

Polished sections of the above three specimens were made, and all show

isotropic "maghemite" as the main constituent, with a few small irregular grains of ilmenite, and some limonite along the cracks and crystal margins (Fig. 4).

TABLE 5

CHEMICAL ANALYSES OF TITANOMAGHEMITES, WITH A RECALCULATION INTO END-MEMBERS

	1		2	3	4	5
FeO	7.87		16.43	2.59	5.00	7.09
MgO	1.05		1.12	0.78	traces	n.d.
MnO	0.24		0.37	0.15	0.45	n.d.
CaO	0.70		n.d.	0.39	0.40	n.d.
Fe_2O_3	64.92		63.76	73.78	73.75	71.51
Al_2O_3	<0.01		1.42	3.41	1.40	n.d.
V_2O_3	2.40		n.d.	1.30	—	0.99
Cr_2O_3	<0.01		n.d.	0.33	0.35	—
TiO_2	19.45		15.50	13.00	15.20	9.60
SiO_2	1.60		0.50	2.02	0.70	n.d.
H_2O	n.d.		1.34	2.12	1.05	n.d.
Rem.	—		—	0.07	2.10	—
Total	98.23		100.44	99.94	100.40	89.19
Recalculated compositions (wt. %)*						
	a	b				
$CaO.SiO_2$	1.45	1.45	—	0.81	0.81	—
$MgO.SiO_2$	1.41	1.41	0.80	1.91	—	—
$FeO.SiO_2$	—	—	—	0.92	0.53	—
$MgO.Al_2O_3$	—	—	2.00	—	—	—
$FeO.Al_2O_3$	—	—	—	5.74	2.44	—
$MgO.Fe_2O_3$	2.38	2.38	1.00	—	—	—
$MnO.Fe_2O_3$	0.78	0.78	1.15	0.46	1.39	—
$FeO.V_2O_3$	3.55	3.55	—	0.67	—	1.33
$FeO.Cr_2O_3$	—	—	—	—	0.45	—
$FeO.TiO_2$	5.00	14.20	29.49	—	7.59	13.98
$FeO.Fe_2O_3$	14.01	—	7.87	—	—	—
$Fe_2O_3.H_2O$	3.50**	3.50	9.35	13.88	7.12	—
γ-Fe_2O_3	49.70	59.36	48.55	62.28	66.72	71.68
TiO_2	16.78	11.95	—	13.00	11.20	2.24
Total	98.56	98.58	100.21	99.67	98.25	89.23
Molecular ratio FeO:TiO_2	0.45		1.17	0.22	0.37	0.82

1. Titanomaghemite from Bon Accord, North of Pretoria, Transvaal, S. Africa. Analyst, H. B. Milner (new analysis—S 542).

2. Titanomaghemite from Bon Accord, Transvaal, S. Africa. Analyst, M. C. Haller (Walker, 1930, p. 17).

3. Titanomaghemite from Bushveld Complex, S. Africa. Analyst, Liebenberg and Haumann (Schwellnus and Willemse, 1943, p. 30).

4. Titanomaghemite from the western part of Onerstepoort, Bushveld Complex. Analyst, H. G. Weall (Wagner, 1928, p. 31).

5. Titanomaghemite free from ilmenite laths (partial analysis), from North of Pretoria, Bushveld Complex. Analyst, G. W. Grainger (Frankel and Grainger, 1941, p. 104).

* a, b are the two possible methods of calculation of the norm of the analysis no. 1 ("a" shows only the 5% ilmenite which appeared in the polished sections and in the X-ray photographs, in "b" all the FeO is calculated as hypothetical γ-$FeTiO_3$).

** Calculated approximately from the amount of limonite observed in the polished sections.

Chemical analysis of specimen 542 (Table 5, Col. 1a), also show a much higher percentage of TiO_2 than is necessary to form the amount of ilmenite actually present. Frankel and Grainger (11, p. 104) gave a partial chemical analysis of maghemite from the Bushveld Complex containing 9.6% TiO_2 (Table 5, Col. 5) but which was free from ilmenite laths. As this excess TiO_2 is only normative and no rutile, anatase, brookite or other titanium minerals were detected neither in the polished sections nor in the X-ray powder photographs, it must be present in the maghemite molecule; the homogeneous maghemite in this case is called titanomaghemite. Thus in the Bon Accord titanomaghemites, while part of the titanium is present in the ilmenite inclusions, most of it occurs in solid solution in γ–Fe_2O_3.

Two possibilities have been suggested to account for the presence of TiO_2 in the homogeneous titanomaghemites in general. The first is the assumption that the excess titanium is trivalent and the Ti_2O_3 may exist in a cubic γ-form isomorphous with γ–Fe_2O_3 (2, p. 92). According to Jakob (18) one may regard titanium as trivalent, instead of tetravalent, in calculating the ilmenite molecule, and then add equal molecular amounts of ferric oxides; the net result would be the same. All the published analyses of titanomaghemite show a certain content of FeO which is interpreted, in this case, as the product of reduction of Fe_2O_3 in the course of oxidation of Ti_2O_3 to TiO_2 during the initial chemical attack of the analytical procedure. Such an assumption, although possible in certain analyses of titanomaghemites, e.g. in Walker's analysis of the Bon Accord specimen (Table 5, analysis 2), yet recalculation of other analyses that shows a molecular percentage of TiO_2 much higher than of FeO (Table 5, analyses 1, 3, 4, 5) cannot be explained in this way. Stscherbina (35) in discussing the significance of oxidation potential in geochemistry gave good reasons why considerable contents of Ti^{3+} and Fe^{3+} are unlikely to occur together in the same mineral.

The second possibility for the interpretation of the composition of titanomaghemites is the possibility of the presence of cubic γ–$FeTiO_3$ in solid solution with γ–Fe_2O_3. Dunn and Dey (8, p. 160) were the first to suggest that at high temperatures Ti can take the place of Fe atom in γ–Fe_2O_3 cubic lattice resulting in a cubic $FeTiO_3$ isomorphous with magnetite and maghemite. This hypothetical γ–$FeTiO_3$, which has not yet been found in nature or prepared synthetically, is supposed to have a defect lattice structure (6, 25) and stands in the same relationship to ilmenite that γ–Fe_2O_3 does to hematite. Nicholls (25, p. 144), during his theoretical discussion on the phase-change-relationships of the iron-titanium oxide minerals suggested that the replacement of $2Fe^{3+}$ by Fe^{2+} Ti^{4+} in the γ–Fe_2O_3 would be expected to result in an increase in its cell dimensions, while simple replacement of Fe^{3+} (ionic radius 0.67 Å) by Ti^{3+} (ionic radius 0.69 Å) would have a very slight effect. He thus considered the measurement—8.3475 ± 0.001 Å —given by me for the cell-edge of titanomaghemite from Bon Accord, Transvaal (2, p. 77) to support the presence of γ–$FeTiO_3$ in titanomaghemite. However, another possible explanation to this increase of the unit cell dimensions may be the presence of Fe_3O_4 (a = 8.396 Å) in solid solution with the γ–Fe_2O_3 (a = 8.335 Å). Recalculation of the analysis of the Bon

Accord titanomaghemite showed about 14 percent Fe_3O_4 together with about 7 percent of other spinels (Table 5, Col. 1a). Even when all the TiO_2 content was recalculated as γ–$FeTiO_3$, an excess of FeO may appear, as in Walker's analysis (Table 5, Col. 2) where it corresponded to 9.35% Fe_3O_4, in addition to about 4 percent of other spinels.

Vincent and his co-workers (39, p. 642) considered homogeneous titanomaghemites to be solid solutions between γ–Fe_2O_3 and γ–$FeTiO_3$ and also using my above measurement for the cube-edge of Bon Accord titanomaghemite extrapolated to a cube-edge of 8.39 to 8.40 Å for γ–$FeTiO_3$. Such extrapolation is of course not accurate, for it is based on a wrong interpretation of the composition of the Bon Accord titanomaghemite. A recalculation of the chemical analysis on the supposition that all the FeO content is present as γ–$FeTiO_3$ and not as Fe_3O_4 (Table 5, Col. 1b) still shows a considerable excess of TiO_2 (about 12%). Similar recalculation of other analyses of titanomaghemites reported in the literature, also show an excess of TiO_2 than was necessary to combine with all the FeO present to form $FeTiO_3$ (Table 5, Cols. 3, 4, 5). Thus, the suggestion of solid solution between γ–Fe_2O_3 and γ–$FeTiO_3$, although possible in principle, cannot solve all the variations in the composition of titanomaghemites.

When the weight percentages of γ–Fe_2O_3 and (Fe, Mg, Mn)O. $(Fe, V)_2O_3$ in 1a and 1b were calculated, ignoring the other molecules appearing in the norm, and then plotted in Fig. 1 against the cell-parameter 8.3475 Å, the two points fall on either side of the line AB′ and at equal distance from it. Although the effect of the TiO_2 and γ–$FeTiO_3$ contents on the lattice parameter is not taken into account, yet the positions of the two points in Figure 1 may suggest that the Bon Accord titanomaghemite may be intermediate in composition between the two possible norms 1a and 1b.

On studying some of the more reliable published analyses of the Bushveld titanomaghemites, the author noticed some striking variations in their FeO content, as well as in the molecular ratio $FeO:TiO_2$, which ranged from about 0.2 to about 1.2 (Table 5). On careful recalculation of the compositions, it was found that although in some cases the FeO content was sufficient to form both $FeTiO_3$ and Fe_3O_4 (Table 5, analysis 2), in others it was not enough to combine with all the TiO_2 molecule even when no magnetite was supposed to be present (Table 5, analyses 1b, 4 and 5), while in still others there was a difficiency of FeO that neither $FeTiO_3$ nor Fe_3O_4 was formed (Table 5, analysis 3). The following compositions of the homogeneous titanomaghemites are thus possible: 1) γ–Fe_2O_3. Fe_3O_4. γ–$FeTiO_3$, 2) γ–Fe_2O_3. γ–$FeTiO_3$, 3) γ–Fe_2O_3. γ–$FeTiO_3$. TiO_2, and 4) γ–Fe_2O_3. TiO_2.

Such variation in composition of specimens from the same locality can be attributed to different degrees of oxidation of the original titanomagnetite. The author has been able to prove that intermediate stages in the oxidation of magnetite to maghemite do occur in nature, and it is thus not illogical to assume that corresponding stages in the oxidation of titanomagnetite may take place to titanomaghemite. The Bushveld titanomaghemites occur in the so-called titaniferous magnetite segregation in the upper part of the norite zone of the Igneous Complex (40). Frankel and Grainger (11)

described inclusions of magnetite and ilmenite laths in their titanomaghemite specimens and suggested that the alteration of the original "titanomagnetite" may not be quite complete. The author suggests that the original homogeneous titanomagnetite belongs to the Fe_3O_4 – γ–$FeTiO_3$ binary series (titanomagnetite II of Chivallier and Girard, 5) and not to Fe_3O_4 – Fe_2TiO_4 series. Gradual oxidation takes place according to the following possible scheme:

1) Fe_3O_4 – γ–$FeTiO_3 \rightarrow \gamma$–$Fe_2O_3 . Fe_3O_4$
$- \gamma$–$FeTiO_3 \rightarrow \gamma$–$Fe_2O_3 - \gamma$–$FeTiO_3$.

On further oxidation at relatively higher temperatures, it is possible that the γ–$FeTiO_3$ will start to be oxidized into γ–Fe_2O_3 and TiO_2, while still in solid solution. Similar oxidation, but of α–$FeTiO_3$, was observed by the author when on heating finely powdered ilmenite in air at 520° C for 38 hours it was transformed into hematite and brookite (2, p. 102), according to the equation:

$$4(FeO . TiO_2) + O_2 \xrightarrow{520^\circ\ C} 2Fe_2O_3 + 4TiO_2$$

Thus the second stage in the oxidation of titanomagnetite to titanomaghemite may take place according to the following scheme:

2) γ–Fe_2O_3 – γ–$FeTiO_3 \rightarrow \gamma$–$Fe_2O_3$
$- \gamma$–$FeTiO_3 . Fe_2O_3 . TiO_2 \rightarrow \gamma$–$Fe_2O_3 - TiO_2$.

It is therefore, possible to consider titanomaghemites as representing a series of minerals ranging in composition from γ–$Fe_2O_3 . Fe_3O_4$ – γ–$FeTiO_3$ to γ–Fe_2O_3 – TiO_2; the exact composition depending on the following main factors: 1) the composition of the original titanomagnetite, 2) the temperature and degree of oxidation, 3) the rate of cooling, and 4) the presence of foreign ions as stabilizers. Such changes are generally taking place below 550° C;[5] at higher temperatures the titanomaghemite is inversed into titanhematite and ferriilmenite which may unmix on slow cooling into hematite-ilmenite-rutile intergrowths. Such ex-solution intergrowths have been observed by Edwards (9, p. 54) and by Ramdohr (29, p. 4). Titanomaghemites may represent the cubic γ-form of the corresponding rhombohedral ferriilmenite series. It is interesting to note that a similar surplus of TiO_2 over the ilmenite and hematite molecules has been obtained on recalculation of the chemical analyses of many homogeneous ferriilmenites (2, p. 121–122). Further work is needed to elucidate the structure of titanomaghemite and to determine how the TiO_2 could be installed in the cubic γ–Fe_2O_3 – γ–$FeTiO_3$ spinel structure as well as in the α–Fe_2O_3 – α–$FeTiO_3$ rhombohedral lattice.

Lastly, it may be noted that the V_2O_3 content in the titanomaghemite from Bon Accord, Transvaal (Table 5, analysis 1) is relatively high (2.40%) which may justify its classification as "coulsonite"; a name originally given

[5] No data is available, however, on the effect of the introduction of Ti^{4+} in the γ–Fe_2O_3 structure on the temperature of inversion of titanomaghemite.

by Dunn and Dey (8, p. 132) for a vanadium-bearing titaniferous iron ore containing 0.5 to 7% V_2O_3. It should be pointed out, however, that the name "coulsonite"—if it has to be used at all—should be restricted to vanadomaghemite with the formula $(Fe, V)_2O_3$, and not to vanadomagnetite as given in the 7th. edition of Dana's System of Mineralogy (7, p. 702). The description given by Dunn and Dey for the original mineral from Singhbhum, India, can be applied fairly well to maghemite.

CONCLUSIONS

In the system γ–Fe_2O_3–Fe_3O_4 all the stages in the oxidation of magnetite to maghemite may occur in nature and may account for some of the considerable differences in the data on the physical properties of magnetite and its appearance in polished sections. The intermediate substances—the maghemomagnetites and magnetomaghemites—are not uncommon, but may have been wrongly identified as magnetite, maghemite, hematite, or mixtures of the former and either of the last two minerals. Their occurrence can only be determined, with certainty, when the carefully separated magnetic minerals, the homogeneity of which is established with X-ray diffraction and microscopic methods, are chemically analyzed in detail and accurate measurements of the cell-edge are carried out. The lattice parameters of magnetite decrease continuously with the progressive increase of its oxidation to maghemite. Substitution in the magnetite lattice by Mg^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+} and Al^{3+}, which may also cause a decrease in its cell dimensions, is of minor importance, either because the cell dimensions of the resultant spinel are not much different from those of pure magnetite or because the extent of substitution is very limited in natural ores.

Fine-grained natural magnetite is oxidized first to γ–Fe_2O_3–Fe_3O_4 solid solution, which is changed at higher temperatures to the more stable α–Fe_2O_3; the remaining Fe_3O_4 in the interior of the grains is also oxidized, directly, to α–Fe_2O_3 at temperatures higher than 500° C. The presence of foreign atoms, e.g., Al^{3+} and Mg^{2+} in the original magnetite structure, has a stabilizing effect on the substituted magnetomaghemite or maghemite thus formed. Rapid cooling may also be necessary for the preservation of the γ–Fe_2O_3–Fe_3O_4 solid solutions.

Most of the maghemites reported in the literature are either magnetomaghemites or titanomaghemites; the term maghemite should be restricted to natural minerals with composition almost exactly γ–Fe_2O_3 and with cell-edge about 8.335 A. Titanomaghemites are homogeneous minerals containing appreciable amounts (more than 2%) of TiO_2 in their γ–Fe_2O_3 spinel structure. They are possibly formed by the oxidation of an original titanomagnetite with a composition in or near the Fe_3O_4 – γ–$FeTiO_3$ binary series. The great variation in the FeO content and in the ratio $FeO:TiO_2$ in the analyses of titanomaghemites from the Bushveld Complex can only be explained by different degrees of oxidation of the original titanomagnetite. It is suggested that titanomaghemites represent a series varying in composition from γ–$Fe_2O_3.Fe_3O_4$ – γ–$FeTiO_3$ to γ–Fe_2O_3–TiO_2; the position of any member in this series depends mainly on the composition of the original

titanomagnetite and its degree of oxidation. The excess TiO_2 over the γ–$FeTiO_3$ molecule, in the last members of this series, is explained by a partial or complete dissociation and oxidation of γ–$FeTiO_3$ into γ–Fe_2O_3 and TiO_2. There is a possibility, however, that this excess TiO_2 may have been present from the start in the original Fe_3O_4 – γ–$FeTiO_3$ titanomagnetite; a chemical analysis of such a titanomagnetite in a teschenite sill from Gunnedah, New South Wales, is given by Wilkinson (45, analysis 3, p. 446). At temperatures higher than 550° C, the titanomaghemite is inversed into the rhombohedral α-form, i.e., the ferriilmenite and titanhematite which may exsolve on cooling into ilmenite, hematite, and rutile intergrowths.

The assumption that all the titanium in the titanomaghemites may be trivalent and the suggested formula γ–$(Fe, Ti)_2O_3$ cannot be supported since many analyses show a molecular percentage of TiO_2 that is considerably higher than of FeO; a fact that renders it impossible to account for the absence of Ti^{3+} in solution, in such cases. Such assumption is also not in accordance with the oxidation potentials. It is the author's opinion that all the titanium in titanomaghemite is tetravalent in the form of γ–$FeTiO_3$, TiO_2 or both; the trivalent titanium, if it occurs at all, must exist simultaneously with the tetravalent form and in a relatively minor amount. It is hoped that the results of magnetic measurements of these minerals, may throw more light on this problem and on the structure of titanomaghemite in general especially in regard to the position of the excess TiO_2 in the γ–Fe_2O_3 – γ–$FeTiO_3$ cubic lattice.

Maghemites, magnetomaghemites and titanomaghemites are all ferromagnetic and generally show strong polar magnetism. However, no sufficient data is available, at present, on the magnetic properties of these minerals, which will therefore be the purpose of a further study by the author, especially concerning the changes in Curie point and saturation magnetization with changes in chemical composition and lattice parameters. Ferromagnetism of rocks has been mainly attributed to titanomagnetites (Fe_3O_4–Fe_2TiO_4 and Fe_3O_4 – γ–$FeTiO_3$ series) and to a lesser extent to ferromagnetic ferriilmenites (α–$FeTiO_3$ – α–Fe_2O_3). Since ferromagnetic magnetomaghemites (Fe_3O_4 – γ–Fe_2O_3) and titanomaghemites may be more common than has hitherto been assumed, and further, since they are petrogenetically related and associated with magnetites and titanomagnetites, the presence of these minerals must, therefore, always be taken into consideration whenever magnetism of rocks is studied in relation to geophysical phenomena.

At the temperature of formation of igneous rocks, there is a very limited miscibility of α–Fe_2O_3 in magnetite, about 8 percent, which increases rapidly above 1,100° C, reaching about 30 percent at 1,450° C. Natural ex-solution intergrowths of hematite in magnetite are very rare and their proportion is generally in agreement with the results obtained from synthetic preparations.

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THE ALTERATION OF MALAYAN ILMENITE GRAINS AND THE QUESTION OF "ARIZONITE"[1]

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ABSTRACT

Examination of ilmenite grains occurring in the alluvium of Malaya confirms the work of various authors in that this mineral undergoes weathering processes that result in a standard progression of alteration from pure ilmenite to a mixture of rutile and hematite (or any related titanium and iron oxide minerals).

A correlation is made of the effects of this alteration on the chemical, physical, and optical properties of the mineral. In the Malayan material two distinctly recognizable phases are present. In the first phase the ilmenite has undergone little, if any, alteration. In the second phase the ilmenite structure has broken down and the material is amorphous. This phase is recognized by a marked decrease in mass magnetic susceptibility, an increase in TiO_3 and H_2O content, and a high Fe^2/Fe^3 ratio. These changes bear directly upon the mineral's extraction properties and so there is a strong economic reason for distinguishing it from the first phase. It is proposed that the term "hydroilmenite" (after Blomstrand) should be given to this phase and that the term "arizonite" should be retained to indicate the final phase of alteration in which the material has recrystallized into a mixture of titanium and iron oxide minerals.

INTRODUCTION

In 1953 the laboratories staff of the Geological Survey, Federation of Malaya, were asked to analyze a number of "ilmenite" concentrates. These concentrates, which normally would have been extracted magnetically at an early stage of the flow-sheet of a tin-mining property, actually had been rejected by the separator and remained with the cassiterite. Chemical assays gave a value of over 60% TiO_2 and about 25% Fe_2O_3, and electromagnetic separation indicated a reduced mass magnetic susceptibility, similar to columbite.

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TABLE 1

PARTIAL CHEMICAL ANALYSES OF MALAYAN ILMENITES AS RECOVERED FROM THE ALLUVIUM, AND THEIR MAJOR ELECTROMAGNETIC FRACTIONATION

Sample No.	% TiO_2	% FeO	% Fe_2O_3	Magnetically attracted at* (amps)	% of Sample
D-10/16	51.4	26.72	8.14	0.3	15.2
				0.4	62.2
				0.5	17.0
D-10/17	52.8	27.01	7.98	0.3	53.6
				0.4	33.0
				0.5	10.3
D-10/18	54.1	25.62	10.27	0.3	29.7
				0.4	51.4
				0.5	15.6
D-10/19	56.0	6.61	21.70	0.4	22.6
				0.5	40.4
				0.6	31.6
D-10/20	56.6	30.17	7.11	0.3	8.7
				0.4	78.4
				0.5	10.8
D-10/21	57.4	18.53	13.01	0.3	13.8
				0.4	42.5
				0.5	37.3
				**0.6	5.9
D-10/22	60.6	13.80	15.64	0.3	8.0
				0.4	34.7
				0.5	44.8
				0.6	7.0
D-10/23	63.0	3.88	24.27	**0.4	8.6
				0.5	37.7
				0.6	48.9
D-10/24	52.6	38.36	4.15	0.3	82.3
				0.4	16.1
D-8/30	64.5	1.15	26.19	0.5	24.2
				0.6	64.4
				0.7	8.7
G-10/1	66.8	2 (approx)	23 (approx)	0.4	9.4
				0.5	32.8
				0.6	47.6
				0.7	9.8
G-8/4	62.8	1.84	26.17	0.4	6.3
				0.5	34.8
				0.6	53.4
				0.7	4.4

* Side slope 25°. Forward slope 15°.
** Insufficient material for inclusion in Table 2.

These properties did not fit any known mineral species, the nearest being "arizonite" (1). A search through the literature indicated that the Malayan material was similar to the material described by Overholt et al. (2), and it was decided to effect a full investigation into the alteration of Malayan ilmenite.

Accordingly a series of ilmenite concentrates was selected on the basis of the TiO_2 content of the bulk sample. Twelve samples were taken with the TiO_2 ranging from 51.4 to 66.8 percent (Table 1). Each sample was subsequently separated electromagnetically on a Frantz Isodynamic separator, using a side slope of 25° and a forward slope of 15° at runs varying by 0.1 amps. Each fraction was further cleaned by hand-picking and where there was sufficient material the fraction was split in half, one-half being used for chemical analysis and the other half being retained for various physical and optical tests, including x-ray diffraction photographs, examination in polished sections, and hardness and density determinations.

CHEMICAL DATA

All the chemical analyses were made by Mr. G. M. Harral, Assistant Director (Geochemistry), and Mr. Leong Pak Cheong, Chemist, Geological Survey, Federation of Malaya. Thirty-seven fractions were supplied for assaying for TiO_2, FeO, and Fe_2O_3 and, where there was sufficient material, for H_2O. In addition the MnO content and insolubles (tourmaline and garnet) were obtained on six of the samples as the four primary constituents gave a consistently low summation. The results are given in Table 2.

PHYSICAL AND OPTICAL DATA

Streak.—The color of the crushed powder was noted for each fraction analyzed. The color ranges from black for the highly magnetic material to fawn for the least magnetic material. The colors are listed in Table 2.

Density.—Density determinations were made on a number of grains from nine magnetic fractions, using the Berman balance "powder" method. Results are given in Table 3.

External Form, Color, and Luster.—The bulk of the grains are irregular and rounded, but a large number of them occur as rhombohedral crystals. This is the same for all the magnetic fractions. The color and luster, however, vary distinctly. In the highly magnetic fractions the grains are deep black with a high metallic luster. As the mass magnetic susceptibility decreases, the grains typically become dull with a reddish tinge. In a few cases, as in sample G-8/4, the grains are silvery-gray and resinous (i.e. "leucoxene").

Hardness.—Using a micro-hardness tester on a Vickers Projection microscope the hardness of grains in eight magnetic fractions was obtained with loads of 50 gm and 100 gm. The results are given in Table 3. It is interesting to note that Nakhla (3) gives HV values of 1027 and 1018 for 50 gm and 100 gm loads respectively for ilmenite.

TABLE 2

CHEMICAL ANALYSES OF ELECTROMAGNETICALLY SEPARATED FRACTIONS OF MALAYAN ILMENITES

Sample No.	Magnetically attracted at (amps)**	% TiO_2	% FeO	% Fe_2O_3	% H_2O	% MnO	% Insolubles	Color of powder
D-10/16a	0.3	53.5	36.29	5.65	n.d.	n.d.	n.d.	Very dark gray
D-10/16b	0.4	55.3	31.54	7.74	0.77	n.d.	n.d.	Dark gray
D-10/16c	0.5	58.95	15.03	19.54	n.d.	n.d.	n.d.	Brownish-gray
D-10/17a	0.3	54.3	34.25	6.48	0.49	n.d.	n.d.	Dark gray (bright)
D-10/17b	0.4	57.2	25.23	11.32	1.31	n.d.	n.d.	Dark gray (dull)
D-10/17c	0.5	59.1	15.59	16.37	2.58	n.d.	n.d.	Brown
D-10/18a	0.3	54.7	33.69	6.79	0.70	n.d.	n.d.	Dark gray-black
D-10/18b	0.4	59.4	19.76	13.81	2.54	n.d.	n.d.	Dark gray
D-10/18c	0.5	63.3	7.54	20.52	n.d.	n.d.	n.d.	Light gray brown
D-10/19b	0.4	57.5	18.12	18.30	1.34	n.d.	n.d.	Brown (Mauvish)
D-10/19c	0.5	61.9	2.56	27.72	2.73	n.d.	n.d.	Light brown
D-10/19d	0.6	64.9	trace	26.27	3.68	n.d.	n.d.	Fawny-brown
D-10/20a	0.3	53.3	38.51	4.79	0.10	n.d.	n.d.	Dark gray
D-10/20b	0.4	55.7	32.54	6.23	1.20	3.74	0.48	Dark gray
D-10/20c	0.5	62.3	12.43	16.69	3.10	n.d.	n.d.	Brown
D-10/21a	0.3	54.2	32.18	5.99	n.d.	n.d.	n.d.	Dark gray
D-10/21b	0.4	56.6	23.42	10.54	1.38	n.d.	n.d.	Dark gray
D-10/21c	0.5	61.5	6.82	21.96	n.d.	n.d.	n.d.	Light brown
D-10/22a	0.3	54.5	33.84	6.15	n.d.	n.d.	n.d.	Dark gray
D-10/22b	0.4	59.1	21.12	11.90	2.52	3.94	0.60	Dark chocolate-brown
D-10/22c*	0.5	63.7	4.96	22.04	4.26	3.24	0.40	Brown
D-10/22d*	0.6	63.6	3.74	20.44	4.57	2.53	1.88	Very light brown
D-10/23c	0.5	63.2	3.09	25.63	3.05	n.d.	n.d.	Brown
D-10/23d	0.6	64.7	0.53	26.16	3.10	n.d.	n.d.	Light brown
D-10/24a	0.3	52.8	40.16	3.51	0.09	2.76	0.38	Black
D-10/24b	0.4	53.3	37.72	4.31	0.37	n.d.	n.d.	Dark gray-black
D-8/30c	0.5	62.8	2.51	28.02	3.00	n.d.	n.d.	Light brown
D-8/30d	0.6	65.8	0.19	27.53	3.38	n.d.	n.d.	Fawny-brown
D-8/30e	0.7	65.8	0.65	24.91	3.91	n.d.	n.d.	Fawn
G-10/1b	0.4	58.2	19.97	15.09	1.64	n.d.	n.d.	Dark chocolate-brown
G-10/1c	0.5	62.4	4.17	25.39	n.d.	n.d.	n.d.	Light brown
G-10/1d	0.6	64.9	0.43	26.43	4.04	n.d.	n.d.	Fawn
G-10/1e	0.7	65.5	trace	23.63	4.12	n.d.	n.d.	Fawn
G-8/4b	0.4	60.2	14.51	18.52	n.d.	n.d.	n.d.	Chocolate-brown
G-8/4c	0.5	64.1	2.36	27.24	2.93	n.d.	n.d.	Light brown
G-8/4d	0.6	66.2	trace	26.46	3.44	n.d.	n.d.	Fawny-brown
G-8/4e*	0.7	66.2	nil	25.15	3.65	1.66	1.00	Fawn

* Remainder mainly rare earth oxides and phosphorous pentoxide (xenotime).
** Side slope 25°. Forward slope 15°.
n.d. = not done.

Examination of Polished Sections.—Eight fractions, obtained with current strengths ranging from 0.3 amps to 0.7 amps, were examined in polished section. The results are given in Table 3. The 0.3 and 0.4 amps material was typical ilmenite, with a moderate reflectivity, no internal reflection and strong anisotropism ranging from light off-white to dark gray in four positions per complete revolution (Fig. 1). In the 0.5 amps material the reflectivity is much lower, there is no pleochroism, and the material has a reddish internal reflection with a metallic "mottled" effect due to what appears to be disseminated specks. The less magnetic material is similar except that the "mottling" is reduced (Figs. 2, 3, and 4).

X-ray Powder Data.—Using a camera of diameter 114.83 mm with Mn-filtered iron radiation, Fe − Kα = 1.9373, x-ray powder patterns were obtained on a number of fractions. The results are summarized in Table 3. The more magnetic material gave perfect ilmenite patterns. The less magnetic material gave diffuse rutile patterns, indicating it to be in an amorphous

TABLE 3

PHYSICAL AND OPTICAL PROPERTIES OF MALAYAN ILMENITES

Sample No.	Magnetically attracted at (ampe)*	Equivalent mass magnetic susceptibility ($\times 10^{-6}$ c.g.s.)	Density	Hardness				Appearance in polished section	X-ray powder pattern
				50 gm load		100 gm load			
				d**	HV	d**	HV		
D-10/17a	0.3	93.92	—	5.0	593	—	—	Typical ilmenite	—
D-10/24a	0.3	93.92	4.57	5.0	593	8.0	464	Typical ilmenite	Ilmenite
D-10/24b	0.4	52.83	4.55	—	—	—	—	—	Ilmenite
D-10/24c	0.5	33.81	4.14	—	—	—	—	—	Diffuse rutile
D-10/20b	0.4	52.83	—	5.0	593	—	—	Typical ilmenite	—
D-10/22c	0.5	33.81	—	5.0	593	—	—	Low reflectivity. Red internal reflection with a metallic mottling effect	—
D-8/30c	0.5	33.81	3.96	—	—	—	—	—	Diffuse rutile
D-8/30d	0.6	23.48	3.81	—	—	—	—	—	—
D-8/30e	0.7	17.25	3.88	5.0	593	7.0	605	As D-10/22c but less mottled	Diffuse rutile
G-8/4c	0.5	33.81	—	5.0	593	—	—	As D-10/22c	—
G-8/4d	0.6	23.48	3.96	5.0	593	—	—	As D-8/30e	Diffuse rutile
G-8/4d 1100°C	0.8	13.21	—	—	—	—	—	As D-8/30e	Rutile + pseudo-brookite
G-8/4f	0.8	13.21	3.88	—	—	—	—	—	—
G-8/4g	0.9	10.44	3.83	—	—	—	—	—	Diffuse rutile
G-10/1c	0.5	33.81	—	—	—	—	—	—	Diffuse rutile
G-10/1c 1100°C	?	?	—	—	—	—	—	—	Rutile + pseudo-brookite
D-10/19d	0.6	23.48	—	5.0	593	—	—	As D-10/22c	—

* Side slope 25°. Forward slope 15°.
d = Mean diameter of indentation (1 unit = 2.5 microns).
HV = Vickers hardness number.
** Mean of three readings.

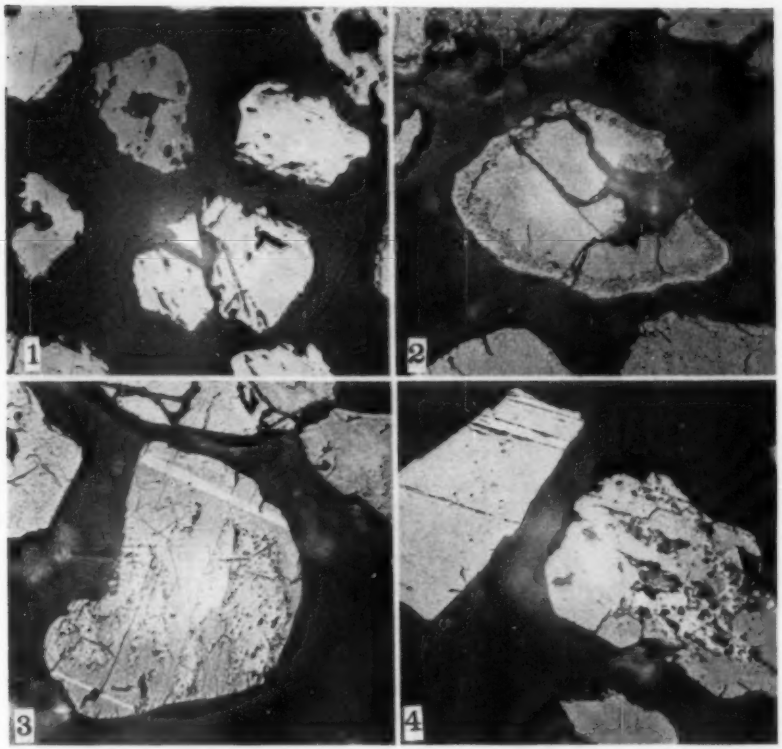

FIG. 1. D-10/24a. Phase 1 material. Normal ilmenite showing pleochroism in off-white and gray (x-nicols) (× 140).

FIG. 2. D-10/22c. Phase 2 material, showing peripheral alteration of a grain (x-nicols) (× 135).

FIG. 3. D-10/22c. Phase 2 material, with unaltered ilmenite (light) remaining along crystallographic planes (x-nicols) (× 135).

FIG. 4. D-8/30e. Phase 2 material, with unaltered ilmenite (light) remaining along crystallographic planes and randomly distributed within a grain (x-nicols) (× 130).

state. This was confirmed by taking a powder photograph of a single rhombohedral crystal mounted, uncrushed, in the powder camera.

An attempt was made to recrystallize this material by heating sample G-10/1c. At a temperature of 880° C no change took place. On heating at 1100° C for four hours a sharp powder pattern was produced which was a mixture of rutile and pseudobrookite. Material from sample G-8/4d ("leucoxene") was also heated at 1100° C for four hours, with a similar result. The powder data for these two heated samples is given in Table 4.

DISCUSSION OF RESULTS

The results of examination in polished section of the material under investigation have established that normal ilmenite can alter, in the solid state, to material that resembles rutile with iron oxide present in a colloidal state, and which retains the rhombohedral form of the ilmenite. This material is similar to the "leucoxene of Stage 3" described by Bailey et al. (4) and the alteration to it proceeds typically from the outer rim of the grain inwards, but also along cracks and crystallographic planes (Figs. 2, 3, and 4).

TABLE 4

COMPARATIVE X-RAY POWDER DATA

G-10/1c 1100°C		G-8/4d 1100°C		Rutile ASTM Card 4-0551		Pseudobrookite (Iron ic titanate) ASTM Card 3-0374	
dÅ (meas.)	I* (visual)	dÅ (meas.)	I* (visual)	dÅ	I	dÅ	I
—	—	—	—	—	—	4.96	33
3.46	4	3.45	8	—	—	3.48	100
3.22	9	3.21	10	3.245	100	—	—
3.14	<1	—	—	—	—	—	—
2.81	<1	—	—	—	—	—	—
2.73	4	2.73	5	—	—	2.74	80
2.475	4	2.471	5	2.489	41	—	—
—	—	2.433	2	—	—	2.45	13
—	—	2.396	2	—	—	2.40	11
—	—	2.318	<1	—	—	—	—
2.280	<1	2.282	<1	2.297	7	—	—
2.175	3	2.177	5	2.188	22	2.20	11
—	—	2.128	<1	—	—	—	—
—	—	2.085	<1	—	—	—	—
2.043	<1	2.045	2	2.054	9	—	—
1.958	2	1.961	3	—	—	1.97	24
1.848	2	1.851	5	—	—	1.86	27
—	—	1.820	2	—	—	—	—
—	—	?	<1	—	—	1.74	13
1.679	10	1.681	9	1.687	50	1.69	1
—	—	?	<1	—	—	1.66	5
—	—	1.631	2	—	—	1.63	8
1.616	2	1.618	3	1.624	16	—	—
1.533	2	1.540 1.533	2 2	—	—	1.54	53
1.477	2	1.478	2	1.480	8	1.49	1
1.448	1	1.449	2	1.453	6	1.46	1
—	—	↓		—	—	1.42	8
1.381	<1			—	—	1.38	5
1.355	2	1.359	5	1.360	16	1.35	7
1.343	1	1.343	4	1.347	7	—	—
↓		↓		↓		↓	
				6 lines to			
				↓			
diffuse		1.093	4	1.0933	4		
↓		↓		↓			
		diffuse					
		↓					

* Maximum strength = 10.

The alteration is accompanied by changes in the chemical, physical and optical properties. These changes are so interdependent that it is difficult to decide in some cases which is the cause and which the effect.

Chemically the main results of the alteration are an increase in TiO_2, Fe_2O_3, and H_2O, and a decrease in FeO. There appear to be two major causes for this. First, there is the oxidation of the FeO giving rise to Fe_2O_3 and probably FeO(OH), both of which would increase at the expense of the FeO. This is accompanied by the second cause, leaching of the iron oxides, the effect being an enrichment of TiO_2. The oxidation process is evident from the data in Table 2. The leaching process is supported chemically by the fact that the percentage of Fe_2O_3 falls far short of the figure obtained by converting the loss in FeO to Fe_2O_3 and the randomly variable values for total iron-oxides obtained.

The physical and optical changes of the properties studied can all be attributed either directly or indirectly to these two causes. The decrease in mass magnetic susceptibility is directly related to the oxidation of the Fe^2 to Fe^3 and to no other factor. A study of figures obtained for various relationships such as Fe^2/Fe^3, Fe^2/Ti, etc., on the electromagnetically separated fractions does not bring out any significant difference amongst the fractions. The relationships all have a similar general trend. Comparison of the samples D-10/19 and D-10/20 as received, however (Table 1), shows that though the TiO_2 content is similar, sample D-10/19, which is much more oxidized, contains much more material with lower mass magnetic susceptibility. The changes in the other properties are indirectly related to the leaching through the secondary cause of the TiO_2 recrystallization. This involves the breakdown of the ilmenite structure into an amorphous state which, in the Malayan material, is recrystallizing to rutile and is the most advanced state of alteration found. Other workers have found that the TiO_2 has recrystallized to anatase and brookite as well, and Overholt et al. (2) have shown in their paper discrediting "arizonite" as a mineral species that a well-defined x-ray powder pattern consisting of a mixture of rutile, anatase and hematite can be produced (A.S.T.M. powder data card 6-0227). A slight inaccuracy is present in that, although the data card states "arizonite" to be "a mixture of hematite, ilmenite, anatase and rutile," there are no ilmenite lines present in the data given for the material. It is interesting to compare this result with the patterns obtained on the two samples heated at 1100° C. This suggests that pseudobrookite is an unstable high-temperature form that breaks down to anatase and hematite and that, had the alteration been proceeding for a sufficient time, the Malayan material eventually may have become a recrystallized mixture of rutile, anatase and hematite.

It is not known how long it takes for the ilmenite to pass into the second and third phases. Presumably this period would vary according to the conditions prevailing, the so-called "tropical-weathering" conditions being the most favorable for large-scale oxidation and leaching. No attempt has been made to determine the reason for the differential geographical distribution in Malaya of the altered ilmenite, which is non-existent in some areas

and commercially abundant in other apparently similar areas. Nor has any attempt been made to examine ilmenite obtained by crushing the parent rock to determine whether the alteration can start before the mineral is released into the alluvium. It is assumed that the ilmenite would undergo a similar degree of alteration as would any other mineral present in the parent rock depending on the weathering processes prevailing.

The maximum TiO_2 content so far recorded in a Malayan ilmenite is 67 percent but, theoretically, complete leaching of the iron oxides is possible giving an end-product that, apart from a few percent of water, would be pure TiO_2.

CONCLUSION

Chemical, optical and physical data for Malayan ilmenite indicate that the ilmenite is being altered, in the solid state, by the normal weathering processes of oxidation and leaching along a standard pattern already recorded by many workers. Two easily identified phases have been recognized in Malaya; a third phase has been described from Arizona.

In the first phase the ilmenite is normal, having a mass magnetic susceptibility of over 50×10^{-6} c.g.s., a well-defined ilmenite structure, and a normal appearance in reflected light. It has a low TiO_2 content and a high FeO content.

In the second phase the mass magnetic susceptibility is less than 40×10^{-6} c.g.s., the structure has broken down into an amorphous state giving a diffuse pattern of rutile (and possibly anatase or brookite), and in reflected light the mineral has lower reflectivity and shows reddish internal reflection with a metallic mottling. The TiO_2 and Fe_2O_3 are high, the FeO almost non-existent, and H_2O is present up to a few percent. The decrease of the mass magnetic susceptibility is sufficiently great to affect the commercial extraction of the second phase material and for this reason it is economically desirable to distinguish it from material of the first phase. The writer suggests the use of the term "hydroilmenite," which was used originally by Blomstrand (5) in 1878, and quoted by Dana (6) in 1892, to describe a titanium mineral from Småland with similar chemical and physical properties. The chemical composition was essentially as follows:

TiO_2	54.23%
FeO	21.91
Fe_2O_3	14.99
MnO	6.34
H_2O	1.33
	98.80

The mineral exhibited rhombohedral form and had a density of about 4. In his paper Blomstrand (5) stated the ore to be

> singular in that it has obviously been exposed to weathering but is apparently unaltered. It is well-known that under atmospheric and moisture influences the mineral may be changed more or less completely to a yellowish-white friable powder consisting principally of titanic acid. It is difficult to explain how a completely

fresh-seeming and unaltered mineral can vary in composition. One cannot certainly determine to what extent moisture content depends on this. It is only certain in my judgment that water is never absent. . . . To signify this in a name, the mineral could be termed a kind of hydrated Ti ore, or, as I suggest, *hydro-ilmenite*, but at the same time, as an apparent by-product, it cannot claim independent existence.

As a logical conclusion, the writer suggests that the term "arizonite" should be retained to indicate the third phase, so far not found in Malaya, in which recrystallization has occurred and a well-defined x-ray powder pattern obtained. The name would be analogous to the terms limonite, bauxite or gummite, and would represent an end-product consisting of titanium oxides (rutile and/or anatase and/or brookite) and iron oxides (hematite) although theoretically there may be no iron oxides.

It is not known at what stage the alteration starts nor the rate at which it proceeds. It is assumed that these depend upon the weathering processes to which the ilmenite is subjected both before and after its release from the parent rock.

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DEPARTMENT OF GEOLOGICAL SURVEY,
FEDERATION OF MALAYA,
Oct. 2, 1958

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SCIENTIFIC COMMUNICATIONS

VOLUME ESTIMATES FROM CONTOURS

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ABSTRACT

Volume estimates by use of contours find their application in many fields. A practical method of computing volumes by use of contours which the author believes of value to geologists is presented here. It is not original, and is one of many such mathematical approaches, but it has a simplicity particularly suited for stratigraphic and economic estimates of masses. It has not appeared in geological journals, and the writer believes that geologists will find it useful in many situations. An example of this method of estimating volumes from contours is given, in terms of ascertaining the "cut" and "fill" necessary to grade a given area, 500 feet by 700 feet, for a 1 percent slope, north to south. A contour interval of 1 foot is used and the map scale is $1'' = 100'$.

INTRODUCTION

THE paper presented here is a method, suitable for the field geologist, of rapidly estimating volumes, by the use of contours. Engineers have long been familiar with the possible solutions to volume problems (1, 2, 3, 4, 5, 7, 8), using in their solutions, contours instead of close surveys, and as discussed in a recent issue of "Photogrammetric Engineering" (6), the Digital Terrain Model, as developed at the Photogrammetric Laboratory of the Massachusetts Institute of Technology, probably offers the most technically advanced approach, using photogrammetry and electronic computers in accurate and large scale solutions to such problems. These aids are generally unavailable to the geological worker not connected with major research institutions. Application of the estimate of volumes from contours to terrain analysis problems is often of immediate and basic concern to many geologists.

The writer first became interested in estimating earthwork volumes when he was employed as a Junior Geologist by the U. S. Corps of Engineers on the Denison Dam project, Denison, Texas, 1939–1940. In 1943, the writer served as an instructor at the Army Engineer School, Ft. Belvoir, Virginia, and became more familiar with the fundamental mathematical approaches to the approximation of earthwork volumes.

Recently, when engaged in an areal geological study, the writer applied what he deems the best of these methods of inferring stratigraphic volumes by geometric consideration, and believes that a paper thereon might be useful to other geological workers, since, so far as he knows, no discussion of this

problem, which must arise in the field for many geologists, has been published in the journals that are readily consulted by geologists and geological engineers. Geological applications of a practical and simple nature may be of the essence of importance in excavation to bedrock that will be suitable for foundations; in stratigraphic and economic quantity determination for borrow pits, quarries, open pit mines, and other types of man made and natural cuts and embankments; in location analysis for highways, railroads, canals, levees, dams, airport and building developments; in location studies for airport approach zones, microwave systems, radar and missile installations, and transmission lines of all types; and in drainage studies related to erosion or silting. Although the contour method is not considered entirely satisfactory for determining the quantity of metalliferous masses where the differences in assay averages within the volume are of critical importance, it is particularly applicable in areas where surface slopes are abrupt and irregular, and where estimates are needed of ore bodies that have a nearly uniform content, such as kaolinitic clay deposits, and uniformly distributed low-grade iron ore occurrences. It is obviously practical in estimating volumes in masses such as mine dumps, tailings, piles, and mill slime, which have a controlled composition, and may be used in estimating volumes of subsurface and surface bodies that are essentially flat-lying and near or at the surface.

One practical, graphic solution of such problems posed by many phases of geological work, requires only a topographic map, or contours drawn directly on aerial photographs, and rapid computations made by geometric constructions, as follows:

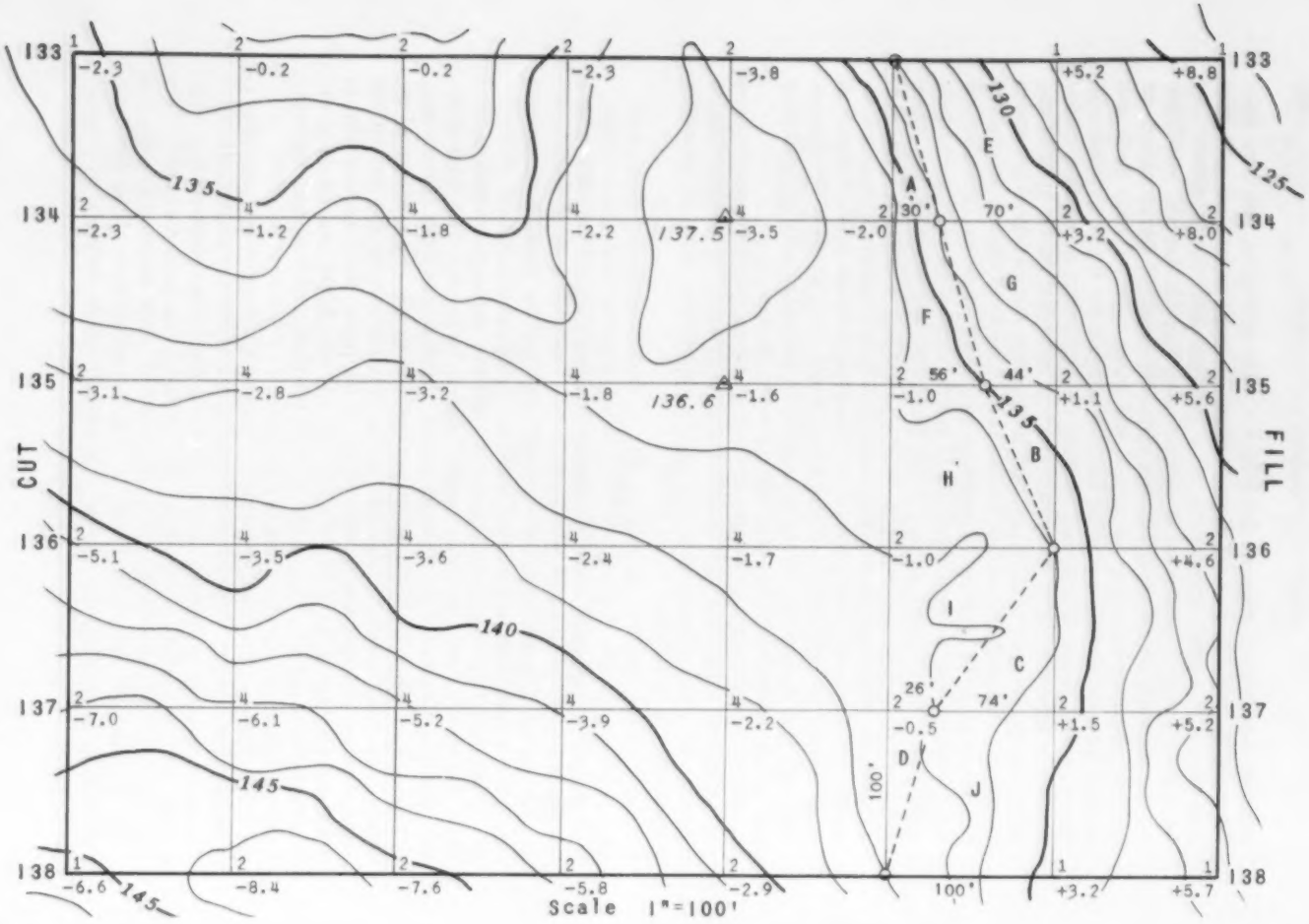
EXAMPLE

Given: A contoured area 500 feet by 700 feet (scale $1'' = 100'$) with a contour interval of 1 foot (Fig. 1).

Required: Compute volumes of "cut" and "fill" to grade the contoured area to a 1 percent slope north to south (top to bottom of map).

Procedure: (1) Divide the area into 100-foot rectangles. The scale of the map is $1'' = 100'$, and the contour interval is 1 foot. The scale of the map is usually selected as the smallest that will accomodate the contour data. The contour interval should be such as will meet the requirements of the degree of detail desired. The size of the example area is 500 feet by 700 feet, but due to expansion or contraction of the paper, the boundary lines of the area may not scale exactly $500' \times 700'$. If such is the case the area may be divided by spanning diagonally between the boundary lines with the scale, and dividing the area into 35 equal rectangles.

(2) The area is to be graded to a 1 percent slope north to south (top to bottom of the map). The boundary lines at the north and south sides of the map are to serve as grade contours at these points. The grade contour indicates the elevation of the ground, after grading has been completed. The numerals 133 and 138 on the north and south are grade contours, and indicate the proposed elevation of these lines. The horizontal lines of the rectangles extending across the map are the intermediate grade contours, at one-foot


CUT
FILL
133
134
135
136
137
138
-2.3
-0.2
-0.2
-2.3
-3.8
+5.2
+8.8
135
130
125
-2.3
-1.2
-1.8
-2.2
137.5
-3.5
-2.0
+3.2
+8.0
A
E
F
G
30'
70'
56'
44'
-3.1
-2.8
-3.2
-1.8
136.6
-1.6
-1.0
+1.1
+5.6
135
B
H
-5.1
-3.5
-3.6
-2.4
-1.7
-1.0
+4.6
140
I
C
26'
74'
-7.0
-6.1
-5.2
-3.9
-2.2
-0.5
+1.5
+5.2
D
J
100'
145
-6.6
145
-8.4
-7.6
-5.8
-2.9
100'
+3.2
+5.7
Scale 1"=100'

h	Σh	FACTOR	PRODUCT	EXCAVATION RECTANGLE A = 10000 sq. ft.
1	8.90	1	8.90	
2	53.20	2	106.40	
4	46.70	4	186.80	

SUM 302.10

$\frac{A}{4 \times 27}$ 92.60

PRODUCT 27,974.46 cu. yds.

h	Σh	FACTOR	PRODUCT	EMBANKMENT RECTANGLE A = 10000 sq. ft.
1	22.90	1	22.90	
2	29.20	2	58.40	

SUM 81.30

$\frac{A}{4 \times 27}$ 92.60

PRODUCT 7,528.40 cu. yds.

TRIANGLE	AREA SQ. FT.	$\frac{A}{3 \times 27}$	Σh	VOLUME CU. YDS. CUT	VOLUME CU. YDS. FILL
A	1500	18.50	2.0	37.00	
B	2200	27.20	1.1		29.90
C	3700	45.70	1.5		68.60
D	1300	16.00	0.5	8.00	
			SUMS	45.00	98.50

TRAPEZOID	AREA SQ. FT.	$\frac{A}{4 \times 27}$	Σh	VOLUME CU. YDS. CUT	VOLUME CU. YDS. FILL
E	8500	78.70	8.4		661.10
F	4300	39.80	3.0	119.40	
G	5700	52.80	4.3		227.00
H	7800	72.20	2.0	144.40	
I	6300	58.30	1.5	87.40	
J	8700	80.60	4.7		378.80
			SUMS	351.20	1266.90

TOTALS

Excavation 28,370.66 cu. yds.

Embankment + 5% 9,829.90 cu. yds.

Difference 18,540.76 cu. yds. wasted

FIG. 1.

intervals, between the grade elevations 133 and 138. 134, 135, 136, 137 are such intermediate grade contours.

(3) The next step is to determine and mark the line of zero "cut" and "fill." This line marks the points on the ground surface that are already at the proposed grade and also marks the dividing line between that portion to be "cut," and that portion to be "fill." This line will be found at the intersection of the grade and the ground contour lines. For example, beginning with the grade contour 138, follow this line to its intersection with the ground contour 138. This is one point of no "cut" or "fill." In a similar manner mark the intersection (zero points) of the grade contours 137, 136, 135, 134, 133 with ground contours of the same elevations, respectively.

(4) Draw straight dashed lines connecting the zero points. These lines, passing through certain rectangles, subdivide those rectangles into triangles and trapezoids, which will have to be computed separately from the rectangles. All of the area to the left of this line is above the proposed grade and will have to be excavated or cut, while that to the right must be filled up to the next line.

(5) Assign letters to the triangles and trapezoids formed by the line of zero "cut" and "fill" so that they may be readily identified for computation. On examining the map in Figure 1, it is apparent that there are four triangles and six trapezoids. The triangles are lettered A, B, C, D from top to bottom and the trapezoids as E, F, G, H, I, J. These letters are then entered in the forms at the bottom of Figure 1, in the columns headed "Triangle," and "Trapezoid."

(6) Interpolate the corner elevations, and compute, and mark corner heights. At the corner of each rectangle, triangle or trapezoid the elevation is to be interpolated between the ground contours. The difference between the interpolated elevation and the grade contour is the corner height above or below the proposed grade. For example, the northwest corner of the area lies between the 135 and 136 ground contours, at an interpolated elevation of 135.3 feet. The grade elevation at this corner is 133 feet or 2.3 feet below the ground surface. This indicates a "cut" and the (−) sign is to be prefixed to the figures, thus, − 2.3. This value is placed just below and to the right of the corner.

(7) The above operation is repeated for each rectangle, triangle, and trapezoid, being careful that the proper sign is placed before the figures. All corners to the left of the line of zero "cut" and "fill" will be (−) and those to the right will be (+).

(8) All the information necessary for the computation of the volumes is now at hand. Each rectangle could be figured separately, but it is more convenient to compute all of them in one operation. In order to do this the corners of the rectangles are marked according to the number of times each is used in the computation. For example, each corner will be used as many times as there are rectangles meeting at that corner, as shown in Figure 2. Some corners are common to more than one square, thus c is common to

one, d is common to two, f is common to three, and e is common to four squares, and so on.

(9) The volumes of the rectangular areas may be computed from the formula:

$$V \text{ (in cu. yds.)} = A/4 \times 27(\Sigma h_1 + 2\Sigma h_2 + 3\Sigma h_3 + 4\Sigma h_4),$$

where A = area of common rectangle, $h_1 h_2$, *etc.* = corner heights, Σh_1, Σh_2, etc. = sum of corner heights used once, twice, etc. This expression is conveniently applied in tabular form (Fig. 1). Four forms are shown, one for the excavation (cut) rectangles, one for the embankment (fill) rectangles, and one each for the triangles and trapezoids. Considering the excavation rectangles first, fill in the column headed "h" with the subscript numbers 1, 2, and 4. These are corner heights common to 1, 2, and 4 squares, respectively. There is no corner height common to three squares in this problem. In the second (Σh) column place the sums of the corner heights common to 1, 2,

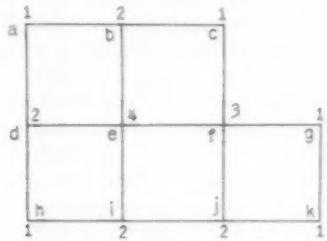


FIG. 2.

or 4 squares as the case may be. The third column is the "factor" column and the numerals 1, 2, and 4 represent the number of squares common to the corner heights h_1, h_2 and h_4. The fourth or "product column contains the products of columns 2 (Σh) and 3 (factor). It is readily apparent that h_2 is represented by a total of 55.5 feet below the ground surface. This value multiplied by the factor of 2 gives 111.0 feet. The values in the products column are then totaled and placed opposite "sum" at the bottom of the column. Solve the expression $A/4 \times 27$ and place the results as a multiplier for the sum previously obtained. This product is the volume of the excavation rectangles, in cubic yards.

(10) In the same manner, and using the form, compute the volumes for the embankment rectangles.

(11) Compute the volumes of the triangular areas. In the first column of the form for triangle computations enter the letters identifying the triangles on the contour map. Compute the area of each triangle and enter in column 2 (area sq. ft.). Required dimensions of the triangles may be scaled from the map. Area of triangle = $\frac{1}{2}$ (base × altitude). Compute the volume for

each triangle and enter in column 3, $(A/3 \times 27)$. In column 4 (Σh), enter the sum of the corner heights for each triangle. Multiply column 3 by column 4 for each triangle and place the products in "cut" or "fill" columns depending on whether the triangle is to the left or right of the zero line. For example, triangle A lies to the left of the zero line, therefore its value is placed in the "cut" column. Triangle B lies to the right of the zero line, therefore its value goes in the "fill" column. Sum up the "cut" and "fill" columns and place the values to the right of "sums."

(12) In a similar manner compute the volumes of the trapezoid areas. Area of trapezoid = $\frac{1}{2}$ (sum of parallel sides $\times$ altitude).

(13) Sum all the excavation quantities and place results opposite the word "excavation" in the lower left hand corner of the form.

(14) The embankment sums must be increased by an amount to allow for shrinkage of the earth in fill. When earth is excavated it swells or expands and its volume is increased as much as 40 percent or even more, owing to its loose and porous condition, but when placed back as fill it will eventually shrink until finally it will occupy less volume than it did before it was excavated. This is due to compaction and the amount of compaction with resulting shrinkage is dependent on the character of the material (coarseness or fineness and/or degree of roundness or angularity), depth of cuts and fills, method of placing the fill, the climatic conditions, and the intensity of loads on fill before stability has been reached. No certain rule can be given for the amount of shrinkage, so that each job must be considered separately. The usual allowance for shrinkage is 8–12 percent. Investigations of the "Bureau of Valuation" of the Interstate Commerce Commission indicate that 9.1 percent is a minimum, and 14.4 percent is a closer final average, for typical estimates. The amount of excavation required to make a given fill may be arrived at by using 1.00 minus the percentage of shrinkage, or 1.00 plus the percentage of fill. Thus, if the shrinkage is 10 percent, divide the fill quantity by 0.90; if the swell is 10 percent, divide the fill quantity by 1.10. For the example problem given here, however, an allowance of 5 percent will be used.

Sum the embankment quantities assuming 5 percent for shrinkage and enter the results according to the above rule after Embankment + 5 percent. This value would be 8893.8 divided by 1.00 minus 0.05 or (0.95) or 936.1 cu. yds. which added to 8893.8 gives 9829.9 cu. yds. total.

(15) The difference between the embankment and excavation will be the amount to be borrowed or wasted. If the fill is greater than the excavation the difference will be made up by borrowing earth from some other place to make up the fill. If the excavation exceeds the fill, there will be an excess of earth which will be wasted.

A summary of the operation is below:

1. Divide area into 100-foot rectangles.
2. Designate grade contours.
3. Determine and mark line of zero cut and fill.

4. Connect zero points with dashed lines.
5. Assign letters to triangles and trapezoids formed by zero line of cut and fill.
6. Interpolate corner elevations and compute and mark corner heights.
7. Lettered triangles and trapezoids are to be computed separately.
8. Mark each corner with number of times it is used in computation.
9. Compute volumes for excavation rectangles and enter in proper form.
10. Repeat for embankment rectangles.
11. Compute volumes for triangular areas.
12. Compute volumes for trapezoidal areas.
13. Sum up all excavation (cut) quantities, from rectangles, triangles, and trapezoids.
14. Sum up all embankment (fill) quantities from rectangles, triangles, and trapezoids, assuming 5 percent for shrinkage (in example) and calculate total yards to be added for shrinkage. Add this to the embankment quantity for total fill.
15. Difference between 13 and 14 is quantity to be borrowed or wasted.

UNIV. OF MISSISSIPPI,
UNIVERSITY, MISS.,
Sept. 17, 1958

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PLASTIC STANDARDS FOR GEOCHEMICAL PROSPECTING[1]

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ABSTRACT

Plastic standards for use in geochemical prospecting have been prepared by impregnating a clear thermosetting resin with different amounts of a stable dye or colored metal complex. The colored plastic is molded or subsequently milled into convenient shapes to form standards that are less bulky and more stable than the liquid standards conventionally used in rapid field methods. The use of such standards is limited only by the availability of stable coloring materials. The preparation of plastic standards for use with copper, zinc, tin, and mercury field procedures is described.

INTRODUCTION

COLORIMETRIC methods for determining traces of metals in soils, rocks, and vegetation are commonly used in geochemical prospecting. Such methods are usually based on the conversion of the metal into a colored compound or complex after a partial decomposition of the sample by hot acids or fusion with suitable fluxes. The colored metal complex is then extracted from an aqueous solution into an immiscible organic solvent, where the intensity of the color or the hue is proportional to the quantity of the metal present. The amount of a particular metal in a sample is estimated by visual comparison of the color of the sample solution with the colors in a series of standard solutions, each member of which contains a known amount of the metal. A standard solution is prepared in a manner identical to that used for the unknown except for the substitution of a solution containing a known amount of the metal for the sample.

Certain aspects of conventional liquid standards often cause difficulties when colorimetric methods are used in rough field laboratories or at sample sites. Many of the color-producing compounds (e.g., metal dithizonates) are unstable when exposed to sunlight and warm temperatures so that sometimes it is necessary to prepare two or more sets of standards in a single day.

[1] Publication authorized by the Director, U. S. Geological Survey.

In addition, some methods require seven or more standards, each in a separate glass tube. This fact makes no trouble when samples are analyzed at a base camp; but because of the bulkiness and fragility of the tubes, handling so many standards is awkward and inconvenient when analyses are made at the sample site. We believe, therefore, that artificial standards free of the undesirable characteristics of the liquid standards have a place in geochemical prospecting.

The use of artificial standards to replace conventional liquid standards in colorimetric chemical procedures is, of course, not new. Various chemical testing kits available on the market include very satisfactory glass color standards; but these glass standards cannot be prepared by an unskilled individual, and kits with such standards are not available for most geochemical prospecting analytical methods.

Artificial standards do not compensate, as do frequently-prepared real standards, for possible changes in color intensity caused by variations in reagent strength and operating conditions. The frequent inclusion of a standard sample with the routine samples, however, provides an adequate check on the reagents and procedure. And if the artificial standards are also occasionally compared with a series of real standards, the chances of introducing any systematic error is slight.

A series of artificial standards in the form of a color chart can be prepared easily and quickly by painting squares on white cardboard to match the colors of the liquid standards in the tubes. Any artist's paint of good quality—water or oil—is satisfactory for producing the desired colors. The results obtained by using such a color chart are reasonably satisfactory. Peive, Sarova, and Rinkis (5) prepared a different type of color standard by applying various India inks to strips of X-ray film from which the emulsion had been removed. Any chart or filmstrip standard must be calibrated, of course, with liquid standards in tubes of the size of those that will subsequently be used to contain the unknowns. The main disadvantage of these types of artificial standards is the difficulty of comparing the color in a layer of liquid with the color on a flat surface. Other obvious disadvantages are that the color charts are not water-proof, and both chart and film are easily torn or frayed.

We thought that if a liquid resin could be permanently dyed to match the colors of the conventional standards and then cast and hardened in tubes of the same dimensions as those containing the standards, most of the implied advantages of artificial standards would be achieved. Such a standard would permit color comparisons to be made under similar geometrical conditions, and the hardened plastic would be resistant to water and rough handling. The purpose of this communication, therefore, is to describe a plastic standard that we have found very satisfactory and that can easily be prepared by an unskilled individual using only simple equipment.

PREPARATION OF PLASTIC STANDARDS

Plastic standards for use with both rapid colorimetric and turbidimetric analytical methods were first developed by Lynd and Turk (2). They used

a transparent thermosetting polyester resin known commercially as "Castolite," which can be dyed in a wide range of colors by adding small amounts of suitable dyes and pigments that are commercially available. At room temperature this plastic is a water-clear syrupy liquid that pours easily and sets to a crystal-clear solid that is extremely durable and resistant to heat and chemicals. A hardener and cold-setting promoter must be used to solidify the syrupy resin. The hardener must be added in a definite ratio to the resin; the amount of cold-setting promoter, however, can be varied depending upon the desired time of hardening and the size of the casting being made.

We used Castolite as did Lynd and Turk; our method of preparation differs from theirs principally in the method of casting, except for the standards for the mercury method. We decided to incorporate all the standards into a single rod, where they appear as a stack of colored discs separated by layers of clear plastic.

Our general procedure for preparing plastic standards is as follows: Conventional liquid standards are prepared first, because the resin must be colored to match them. The matching is done visually. For colorimetric standards that have the same hue but differ only in intensity throughout the range over which standards are prepared, approximately three tablespoonfuls of the clear resin are poured into a paper cup and small amounts of the dye are added to the resin until the color intensity matches that of the liquid standard having the most concentrated color. The remaining plastic standards may be prepared by dilution of this colored resin with appropriate amounts of clear resin. In all cases, however, the various resin standards should be compared visually with each corresponding conventional standard and the color intensity of each adjusted if necessary. For standards that differ in color with different concentrations of metal, each standard must be prepared separately.

After the requisite number of portions of liquid resin have been colored, the laminated rod can be cast in a glass tube of the same dimensions as those containing the standard solutions used as color guides. The tube is clamped in a vertical position and about one teaspoonful of clear resin mixed with the hardener and cold-setting promoter is poured into the tube and the mixture allowed to gel for about 10 minutes. Then the hardener and cold-setting promoter are mixed with the colored resin corresponding to the lowest standard, and this mixture is poured into the tube until the volume of the layer is approximately equal to the volume of the organic layer in the liquid standard. This colored layer is allowed to gel, and then another layer of clear resin is poured on top of the colored layer and allowed to gel. The hardener and cold-setting promoter are then mixed with the colored resin corresponding to the next highest standard and this mixture is then poured into the tube and allowed to gel. This process of pouring alternating clear and colored layers is continued until all of the colored resins have been poured, then a clear layer about three-fourths of an inch thick is poured on top of the last colored layer. After the gelled plastic has cooled to room temperature,[2] the plastic is cured by heating the tube for 30 minutes in a water bath at 70° C.

[2] Some heat is liberated by the plastic as it gels. Unless the plastic is cooled to room temperature prior to curing, the casting will crack while it is being cured.

After it has been cured, the plastic casting can be removed by inverting the tube and tapping its mouth sharply against a solid surface. About 5 ml of acetone added to the tube acts as a lubricant and aids in the removal of the rod. A thin layer of the syrupy resin often adheres to the sides of the rod but this can be removed easily by wiping the rod with cleaning tissue moistened with acetone. If desired, a small clip similar to those on fountain pens can be attached to the top of the plastic rod, which then is truly a pocket standard. The total time required to prepare this type of standard is about five hours.

An alternative to the above method is to cast each colored standard in a separate tube. After having been cured, the plastic rods are removed and sliced into discs about one-half inch thick. These discs can then be cemented between discs of clear plastic to form a rod. This method is particularly useful if one wishes to make a number of identical rods. The optical quality of this type of rod, however, is inferior to that of the homogeneous type previously described.

Copper.—The field method used by the U. S. Geological Survey for the determination of copper in soils and rocks was developed by Almond (1). The method is based on the reaction between 2,2′ biquinoline and copper (I) to form a pink compound. Almond's paper contains a discussion of this analytical method and directions for preparing the liquid standards, which do not differ in hue but vary only in intensity of color over the suggested range of the method.

Although we found no commercially available dye that would satisfactorily duplicate in "Castolite" the color of the copper-biquinoline complex, a complex formed by the reaction of tin (IV) with 4,5-dihydroxyfluorescein (Gallein [3]) gives the resin a red color closely resembling that of a copper standard. The red complex is prepared by allowing stannic ion to react with 4,5-dihydroxyfluorescein in an acetate-buffered aqueous medium at a pH of 2–2.5 (3). The complex is extracted by a binary mixture of o-dichlorobenzene and cyclohexanone; this colored liquid extract is used as the coloring agent for the plastic in both copper standards and tin standards.

The plastic copper standards are made according to the general procedure by first preparing the 6-microgram standard [4] and then diluting portions of this more concentrated standard with clear resin to produce the lower standards. A difficulty encountered in the preparation of copper plastic standards is that the color produced by the tin-fluorescein complex tends to fade slightly during the curing. To correct for this fading, the resin should be of slightly deeper color than the standard it is to match: the necessary correction must be determined experimentally. Once the plastic has been cured, the color is very resistant to fading, however. After exposure of one set of copper standards to the weather for one month, the clear plastic layers were slightly yellow, and the colored layers remained unchanged.

[3] Gallein, Eastman Kodak No. 7453, is the only commercially available product in this country that we have found to give this reaction.

[4] Almond (1, p. 6) suggests a standard series equivalent to 0, 0.2, 0.4, 0.7, 1.0, 1.5, 2.5, 4.0, 7.0, and 10 micrograms of copper; however, the current practice in the Geological Survey laboratories is to use the following series of values: 0, 0.2, 0.4, 0.8, 1.5, 3, and 6.

If the stannic 4,5-dihydroxyfluorescein complex cannot be used as a coloring agent, an alternative—although less satisfactory—method of preparation may be substituted. Another type of thermosetting polyester resin that contains a cobalt compound as a catalyst is commercially available (Polylite). The cobalt compound imparts to the resin a pink color that matches closely the colors of the more dilute copper-biquinoline standards. Artificial standards can be prepared therefore by diluting portions of this concentrated resin to the desired color with colorless styrene monomer, which can be purchased with the resin. Because the catalyst is also the color-producing compound in this resin, the curing time for the different standards varies from about 45 to 90 minutes; once the resin has gelled, however, the curing process can be accelerated by heat. It is not feasible, however, to make a homogeneous rod with this type of resin because of the prohibitively long time required to cure the layers of clear plastic that are used to separate the colored discs. We attempted to produce such a rod by pouring alternate layers of clear "Castolite" and colored layers of the cobalt-containing resin, but were not successful because the different coefficients of shrinkage of the two types of plastic often caused optical aberrations, as well as cracking during the curing process. These difficulties can be overcome by hardening each standard in a separate tube and fabricating the standard rod as described previously by cementing alternate discs of colored and clear plastic.

The cobalt-containing resin rod is less desirable than the one containing the tin complex, because the color of the standards with highest metal content cannot be matched satisfactorily. The deepest color obtainable with the cobalt-containing resin corresponds to that of the standard having only 1.5 micrograms of copper.

To see how plastic standards compared with conventional standards when used in actual analytical work, 5 samples of soil were analyzed for copper and zinc. The sample solutions were matched with both plastic and liquid standards. The results of the copper analyses are shown below; the results of the zinc analyses are given under the section on plastic zinc standards.

DETERMINATION OF COPPER IN SOIL ALIQUOTS

Sample No.	Copper found, in micrograms	
	Plastic standards	Liquid standards
1	0.8	1.2
2	0.4	0.4
3	0.2	0.3
4	0.3	0.4
5	0.4	0.4

Zinc.—The field method of analysis for zinc is based on the reaction of zinc with dithizone to form a zinc dithizonate, which in the presence of an excess of dithizone exhibits a color varying from green to red depending on the amount of dithizone present. A discussion of the procedure and directions for the preparation of the zinc dithizone standards are given by McCarthy and Lakin (4).

The resin "Castolite" and dyes that can be purchased with the resin were

used in preparing the plastic zinc standards. The best results were obtained by using dilute alcohol or acetone solutions of these dyes to color the resin. The dilute dyes can be prepared in the following manner:

DYES

Dilute green	50 mg green dye dissolved in 10 ml acetone.
Dilute blue	4 drops concentrated blue dye in 10 ml acetone.
Dilute violet	4 drops concentrated violet dye in 10 ml acetone.
Dilute red	4 drops concentrated red dye in 10 ml acetone.

The following procedure is used to obtain a fair approximation of the color of the zinc standards.

ZINC STANDARDS

	Amount of dilute dye to add to 1 tablespoonful clear resin	
Standard	No. of drops	Color of dye
Blank	2	Green
1 microgram	1	Green
	4	Blue
	2	Violet
2 micrograms	2	Blue
	5	Green
	2	Red
3 micrograms	7	Violet
	1	Blue
	4	Red
4 micrograms	1	Blue
	7	Violet
	6	Red

The standard rod for zinc is prepared by casting the plastic in a glass tube in the same manner as was done for copper.

Some data on comparative zinc analyses using liquid and plastic standards are given below:

DETERMINATION OF ZINC IN SOIL ALIQUOTS

	Zinc found, in micrograms	
Sample No.	Plastic standards	Liquid standards
1	3.0	3.5
2	2.5	2.5
3	2.0	2.0
4	1.0	1.0
5	1.5	1.5

Mercury.—A field method for the determination of mercury in soils and rocks has recently been developed by Ward (6). This method employs dithizone which reacts with mercury under suitable conditions to form an orange-colored mercuric dithizonate. Ten mercury standard solutions ranging in color from a pale gold to a deep orange are used.

To prepare plastic artificial mercury standards, a saturated ethyl alcohol solution of Orange II is used to dye the resin. To match the standard with the highest metal content about 7 drops of Orange II dye solution in one tablespoonful of clear resin are required. The weaker standards are pre-

pared by dilution of this concentrated standard with clear resin. The standards are cast separately in pointed 15-ml centrifuge tubes to make them the same shape as the liquid standards, which are prepared and used in 60-ml separatory funnels.

Tin.—A field method for the determination of tin in soils and rocks has recently been developed by Marranzino and Ward (3). This method utilizes the reaction of 4,5-dihydroxyfluorescein with tin (IV) to form a colored complex. To prepare plastic tin standards the same procedure used in the preparation of plastic copper standards is followed. The same resin and coloring agent are used; but, of course, the plastic tin standards are calibrated by comparison with liquid tin standards.

APPLICATIONS

The use of plastic standards is by no means limited to the four analytical methods described in this paper, because it is probable that they could be prepared and used in most colorimetric methods requiring colored standards for visual comparison. Conceivably, however, one may wish to use a colorimetric test for which no stable dyes are available. This would be the principal limitation in the preparation of plastic standards.

We believe that plastic standards should be most useful in the following circumstances: In the laboratory their use in those procedures where liquid standards are relatively unstable should increase the productivity of an analyst by eliminating the frequent time-consuming preparation of a series of standard solutions. In the field where analyses are made at or close to the sample site, the substitution of a single unbreakable plastic rod for several standards in fragile and bulky glass tubes should also reduce the time required to make an analysis. Also, and probably most important, this simplification of the analytical equipment should make the field man more willing to use a chemical method in the field, and his efficiency should be increased by having on-the-spot data available for finding and tracking down economically important dispersion patterns of metal in soil and sediment.

U. S. Geological Survey,
Denver, Colo.,
Feb. 4, 1959

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DISCUSSIONS

THE SOURCE BED CONCEPT

Sir: In the article by C. L. Knight entitled, "Ore Genesis—The Source Bed Concept" (ECON. GEOL., v. 52, pp. 808–817) some broad generalizations were made that do not seem to be warranted. The one of greatest importance states: "that sulfide ore bodies in the great majority of mining fields are, or were derived from, sulfide accumulations that were deposited contemporaneously with other sedimentary components at one particular horizon in the sedimentary basin which constitutes the field and that sulfides subsequently migrated in varying degree under the influence of rise in temperature of the rock environment."

Few geologists would doubt that the western United States is one of the great provinces of sulfide ores, nevertheless in that area there is generally an absence of evidence in favor of the "source bed concept."

The writer does not deny that some sulfide ores are syngenetic, for example, the Kupferschiefer of Germany and the White Pine deposit in the Nonesuch shale of Keweenan Point, Michigan, but to say that the great majority of sulfide ores are related to syngenetic sulfides in sediments is another matter.

To confine the discussion to a reasonable length, the geology of a number of the largest sulfide deposits in western United States was reviewed with evidence for or against the source bed concept in mind. In every case definite evidence is lacking that would favor the concept and in all there are indications against it. For convenience the mines or districts are arranged alphabetically.

Aspen.—Ore in this old Colorado district occurred in limestone mainly close to the Silver and Contact faults but also in quartzite. The bodies along and near faults are oriented at nearly right angles to the beds throughout the entire thickness of Leadville dolomite and into the quartzite. The localization of the ore seems to be controlled by porphyry intrusions, faults, and easily replaceable limestone.

Ajo.—The ore occurs in the Cornelia quartz monzonite and its dioritic border facies. There is an absence of sedimentary rocks older than the ore and thus there is a lack of an available sedimentary source bed as far as known.

Bingham.—The huge Utah copper deposit and other large sulfide bodies in adjacent parts of the district are instructive because they occur in both igneous and sedimentary rocks. Copper occurs close to large intrusive bodies and lead-zinc mainly in limestone farther away, but throughout the Paleozoic rocks ranging from Cambrian to Carboniferous in age. Butler and others state, "the age of the sediments, therefore, does not appear to determine their importance as ore carriers." Ore occurs in limestone, quartzite, shale and

porphyry. Boutwell long ago considered the sediments as a possible source and wrote, "Thus the non-occurrence (so far as observed) of cupriferous sulphides in normal unaltered limestone and the great size of the ore bodies throw the burden of proof on those who would maintain their origin by concentration from their original form as sedimentary deposits."

Bisbee.—The great copper, and lesser zinc-lead deposits of Bisbee furnish a strong argument against a "source bed concept" for the district. Large disseminated deposits occur in porphyry but by far the largest production has come from limestones ranging in age from Cambrian to Carboniferous and aggregating around 5,000 feet in thickness. Ore occurs through a vertical range of at least 3,000 feet with concentrations in various horizons in different places. The great Campbell ore body cuts across fully 2,000 feet of beds. There is, moreover, a concentration of the ore around the Sacramento stock and although the sedimentary beds are widely exposed in the Mule Mountains and elsewhere they are generally completely barren, outside of a narrow zone around the stock south of the Dividend fault.

Butte.—It scarcely needs emphasis that this great district lies in an intensely faulted zone in quartz monzonite of the Boulder Batholith and there is a lack of sedimentary rocks anywhere nearby to furnish the source bed.

Castle Dome.—This deposit, though not large by western standards is of interest because it is situated between those at Globe and Miami and that at Superior (Magma Mine). The ore is an area of granodiorite and quartz monzonite intruded by later diabase. Ore does not occur in Paleozoic sediments but is completely isolated in igneous rocks.

Climax.—This huge deposit of molybdenite and lesser sulfides lies west of the large Mosquito fault in an area of granite intruded by Tertiary (?) porphyry dikes. There are schist inclusions in the granite but there are no sedimentary rocks near the deposit, west of the fault. The structural situation is such that there is no reasonable possibility of a source bed having furnished the molybdenum not are there abnormal amounts of molybdenum, as far as known, in the sedimentary rocks of the region.

Globe.—This district, now largely mined out, was highly productive for many years. There the ore occurred mainly in limestone and to a lesser extent in quartzite, but at various horizons in a thick sequence of beds. The ore is clearly related to the Old Dominion fault and was mined parallel to the fault for a length of three miles and 2,200 feet in depth. The maximum distance of ore from the fault was 400 feet. Selective replacement of limestone in preference to quartzite and shale explains the localization.

Jerome.—The main ore body is a pipe-like mass that replaced schistose quartz porphyry along the contact with a diorite intrusion. Rocks and ore are Precambrian in age. The top of the United Verde pipe was down faulted to form the rich united Verde Extension deposit. The United Verde pipe extends over 3,000 feet vertically and the faulted and eroded extension upward probably extended an additional 2,000 feet or more. This huge sulfide pipe seems unrelated to any sedimentary or meta-sedimentary rocks.

Leadville.—The abundant occurrence of ore in the Leadville limestone might be used as an argument in favor of the source bed concept but con-

sideration of other facts seems to eliminate this possibility. The ore ranges from pyrometasomatic near the Breece Hill stock to mesothermal varieties in limestone, porphyry, quartzite, and sandstone. There is a radial arrangement around Breece hill. The Leadville (Blue) limestone is most productive in much of the district, but in the Iron Hill and Carbonate areas the lower White limestone is the most productive. Ore was generally concentrated below impervious barriers rather than along particular beds.

Magma.—The principal production has been from the Magma vein which is along the Magma fault zone. Ore occurs over a vertical distance of 5,000 feet and crosses Precambrian schist, later shale, conglomerate and quartzite up to Mississippian limestone. Diabase is abundant as sills. The limestone was not productive in the Magma vein but has in recent years proved productive to the east beyond another fault. The ore shows little relation to the various wall rocks, but tends to be better in diabase.

Miami.—The copper deposits at Miami are only a few miles from the deposits at Globe, but occur as disseminations in schist where intruded by granite and diabase. There are no sedimentary rocks in the immediate area to act as source beds for the very large amount of copper produced by the Inspiration and Miami mines.

Morenci.—The huge copper deposit now being mined is entirely in porphyry but previously large amounts of ore was mined from garnet zones in limestone and quartzite near the Morenci stock. Ore in limestone occurred over a vertical range of 750 feet and at several horizons. Lindgren states that the deposits are not tied to any particular horizon, but distributed through the whole Paleozoic series. The ore occurred only in and near the igneous rocks.

Park City.—The ore occurs at several horizons in a thick sedimentary series. Butler states that throughout the district a given bed does not seem to be uniformly favorable. Recent work shows that ore occurs over a greater range in the stratigraphic sequence than had been formerly appreciated.

Pioche.—Bedded replacement deposits of zinc and lead occur at the intersections of certain steeply dipping fissures with favorable limestone beds. At the Prince mine there are, at least, six such horizons of bedded replacements one above another. Ore also occurs in the Pioche shale and in limestones above the main productive formation. The ore clearly favors the easily replacement limestones but there is a lack of available evidence that the source of the sulfides was in the limestones.

Ray.—The copper ores at Ray are across a mountain range from those at Globe and Miami but resemble the latter in that the main part of the ore is in the Pinal schist. Lesser amounts occurs in granite porphyry and diabase. There is a lack of sedimentary rocks in the area which could act as source beds.

Santa Rita.—This is a large area containing several kinds of deposits. The largest is the Chino copper mine which has disseminated copper sulfides in granodiorite porphyry. Adjacent to the largest intrusion there are contact metamorphic deposits of magnetite plus sulfides. In the outer zone of the metamorphic auroele are sphalerite deposits, some occurring as upright steep

masses controlled by steeply inclined fissures, some parallel to granodiorite dikes. Blanket-like deposits occur in limestone beneath impervious shale. All of the ores are in, or peripheral to igneous rocks.

Tintic.—This is a classic example of ore in sedimentary rocks, mainly limestone, but related to fissures that cross hundreds, perhaps thousands of feet of beds. Bedding plane replacements occur at many horizons. A single ore shoot crossed limestone beds from the surface to the 700-foot level and below. Ore in one mine followed fractures from near surface to the 2,000-foot level. At places ore crosses from Ordovician to Mississippian beds without essential change. Here too there is a lack of relation to any particular sedimentary beds.

Tombstone.—This district is of interest because it is only 20 miles from the large deposits at Bisbee, which occur in Paleozoic limestone whereas a goodly-percentage of the ore in Tombstone occurred well above the base of the Mesozoic rocks. It occurred not only in limestone but in novaculite and in igneous dikes and is related to faults, dikes and crests of anticlines with little relation to stratigraphy except concentrations below impervious shales.

Knight states that it is illogical to assume a sedimentary origin for one sulfide orebody and to argue that another orebody of very nearly identical mineralogy originated from a magma. Actually there is no compelling reason why they may not have a somewhat similar mineralogy but, as a matter of fact, there are usually striking differences in mineralogy. Many epigenetic ore bodies contain minerals other than sulfides and the wall rocks are commonly highly altered with the consequent development of a variety of minerals. Undoubted syngenetic deposits do not have this complex alteration with accompanying introduction of new elements. Any realistic consideration of the mode of origin of epigenetic ores must take into account the wall rock alteration.

In short, the two modes of origin, syngenetic and epigenetic, are not in opposition but are complimentary.

G. M. SCHWARTZ

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.,
Jan. 19, 1959

THE CLASSIFICATION OF METALLIFEROUS PROVINCES AND DEPOSITS

Sir: May I reply to one or two points raised by Dr. Thomas M. Broderick (ECON. GEOL., vol. 53, p. 1042–1046) in his rather good natured criticism of the above paper.

1. The original paper was published in the Transactions of the Canadian Institute of Mining and Metallurgy (vol. 60, p. 333–335). The version which Dr. Broderick saw had been given some editorial treatment which, perhaps, implied some claims not intended by the author, e.g., I had not meant to

imply that supergene enrichment was unimportant in the formation of porphyry coppers of economic grade.

2. I would not wish to argue with Dr. Broderick concerning the geology of the Keeweenaw peninsula, to the knowledge of which he has contributed so much. However, I submit that the association between native copper and basalts is world-wide, and this cannot be accidental. In many cases, e.g., in the well-known Coppermine District of northwestern Canada, the basalts have not been intruded by granite.

3. Regarding the use of prospector's terms, what I meant to suggest was that a classification depending on field association perhaps has a greater practical value than one based on more theoretical postulates. e.g., assumed temperatures and depths of deposition.

C. J. SULLIVAN

TORONTO, ONTARIO.
February 16, 1959

THE PROBLEM OF THE CARBONATE APATITES

Sir: Despite the absence of any references, G. W. Martin apparently had studied small portions of the literature on carbonate apatites prior to preparing his discussion (ECON. GEOL., v. 53, p. 1046–1048) on the "Mineralogy of phosphatic oolites." He gives the formula for carbonate apatite as $Ca_{10}(PO_4)_6(CO)_3 \cdot H_2O$ [sic]. Whether he really means this or $Ca_{10}(PO_4)_6(CO_3) \cdot H_2O$, he is unquestionably in error.

In either case, he apparently supposes that the crystal structure of apatite contains 28 large anions (O + F + OH), including the oxygen of water. This thesis represents a fundamentally new approach to the crystal chemistry of apatite, and yet it completely fails to indicate how these *extra* two large anions could possibly fit into the lattice $P6_3/m$ in a symmetrical manner. Had he delved into the literature more than superficially, he might have discovered that this formula cannot possibly represent the composition of carbonate apatite and also some of the reasons why it cannot.

Inasmuch as the composition of the "end member" of the francolite-fluorapatite series has never been defined except in terms of francolite itself—certainly it is not $Ca_{10}(PO_4)_6(CO_3) \cdot H_2O$—the mineral compositions under consideration cannot be defined on the basis of invalid speculations concerning an end member that cannot be shown to exist. Indeed, the compositions under consideration approximate those of francolite, a mineral name that has been in use since 1871 without significant modification of its meaning (1).

Martin, presumably relying on Dana's System of Mineralogy, mentions substitution of (CO_3OH) groups for (PO_4) groups in order to obtain carbonate apatite. (This statement, of course, is not consistent with the formula which he gives, because the carbon represents an addition rather than a substitution in his formula.) Were the substitution of (CO_3OH) for (PO_4) a valid representation of the ionic replacements, one hydrogen atom would necessarily enter the structure for each carbon atom. Even the most casual

examination of the five excellent analyses of francolite on record will reveal that no such simple explanation will suffice (2).

Notably, Martin's chemical analyses do not show the carbon dioxide contents of the five samples on which he is presumably presenting new data. Thus his analytical results are quite meaningless with respect to his conclusions. However, based upon extensive experience in the investigation of such substances, I shall re-state his conclusions.

1. The phosphatic mineral of oolites from the Gay mine is francolite.

2. The present writer discarded "collophane" as the name of a mineral species in 1942.

3. The names of minerals of the apatite group cannot be based upon "end members" that have no demonstrable existence. Insofar as is known, compositions closely approaching those of the original samples of francolite and dahllite represent the "end-member" compositions for these carbonate apatites.

4. A mineral substance that contains approximately three percent of carbon dioxide should never be called fluorapatite or hydroxyapatite. The substitution of "carbonatian-fluorapatite" for francolite is entirely inappropriate.

5. No mineralogist has suggested that each possible variation from the general apatite formula should be given a "proper" name—certainly not the present writer.

The inadequacies of Martin's discussion require three additional conclusions.

6. Martin has presented conclusions that impinge on complex crystal-chemical concepts without consideration of relevant data or cogent arguments (4, 5, 6, 7).

7. There seems to be no end to misguided attempts to befuddle the entire problem of the carbonate apatites by inept and inadequate speculations. Some difficult problems exist, such as the manner of precipitation of calcium phosphates in biochemical environments (8), and the radioactivity of phosphatic sediments (9), but considerable time is lost by the necessity for reiteration of fundamental concepts (10, 11, 12).

8. No useful purpose is served by presentation of casual descriptions that disregard existing concepts and nomenclature (3).

DUNCAN MCCONNELL

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Feb. 16, 1959

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ILLINOIS-KENTUCKY FLUORSPAR DEPOSITS

Sir: M. P. Nackowski's abstract "Physical and Chemical Environment of Illinois-Kentucky Fluorspar Deposits" (Econ. Geol., v. 53, no. 7, p. 925) emphasizes the importance of sandstone aquifers superjacent to limestone host rock in localization of flat-lying bedding-replacement fluorspar deposits. Although many of these deposits in the Illinois-Kentucky district do lie below sandstone beds, most are separated from the base of the sandstone by impervious shale or dense limestone, which would minimize dilution of hydrothermal fluids by groundwater contained in the sandstones.

The large massive replacement deposits occur in oölitic to semi-oölitic limestone of high porosity, permeability and purity, subjacent to relatively impure and impermeable dense limestone beds in the Fredonia and Levias members of the Ste. Genevieve formation. Many of these ore bodies have shale roof beds that form the basal portion of the Rosiclare sandstone member of the Ste. Genevieve formation.

Two major disseminated replacement deposits occur in less permeable limestone units near the top of the Renault formation. One of these, the Minerva Mine No. 1, several miles north of Cave-In-Rock, Illinois, is capped by shale or shaly sandstone and locally by a one-foot thick dense limestone bed, which is sandwiched between the back of the ore and the base of the Bethel sandstone. The other deposit, the Shouse-Skelton ore body near Joy, Kentucky, is subjacent to 20 feet of predominantly shale with a few crystalline limestone bands. This impervious section separates the top of the ore from the Bethel sandstone, and is worthy of brief mention:

Normally, above barren limestone, this argillaceous section contains several thin zones of red to maroon shale. Above the ore body, however, and for perhaps 25 feet beyond the edges of the ore, the section contains no trace of red or maroon colors. This marked color change was a valuable ore guide in the exploratory drilling, and is apparently due to heat of mineralization that possibly reduced the red ferric-oxide to black ferrous-oxide in an environment deficient in oxygen.

I do not believe Nackowski's thesis can be substantiated by the evidence offered in most of the mines of the district, nor would it find general acceptance among geologists who have worked there.

William A. Oesterling

Winnemucca, Nevada,
March 19, 1959

ISOTOPIC STUDY OF SOME COLORADO PLATEAU ORES

Sir: In a recent article in ECONOMIC GEOLOGY, Miller and Kulp (1) have closely identified us with ". . . the hypothesis of hydrothermal deposition accompanied by old radiogenic lead from the basement at one time 60 million years ago. . . ." In both our correspondence with Mr. Miller and in our published papers we have:

1. Purposely avoided the use of the word "hydrothermal" in discussions of the origin of the Colorado Plateau deposits.

2. Stated that the source of the original radiogenic lead was ". . . probably to be found at depth" (2, p. 15). We did not limit the source of this lead to the basement, but we do believe that the uranium and much of the radiogenic lead now found in the ore deposits of the Colorado Plateau cannot have been derived from the enclosing Triassic and Jurassic sediments.

3. Stated that ". . . our immediate objective has been to establish the age of the deposits within very broad limits, that is, whether they are Triassic, Jurassic, Cretaceous or Tertiary age" (3, p. 5). We did not limit the age of the deposits to 60 m.y. but noted that the lead uranium ages presented were maximum values, were corrected only for common lead and that additional corrections for original radiogenic lead and selective loss of uranium would reduce the ages given (2, p. 13); (3, p. 9).

Unique ages for the uranium ores of the Colorado Plateau ore are particularly difficult to obtain. The limitations of the analytical data, the sensitivity of the age equations below 100 m.y., and the recent solution and redeposition of uranium and radiogenic lead in some ore specimens all contribute to the problem of setting narrow limits to the discordant ages of the Plateau. However, the lead isotope data does suggest to us that the deposits are epigenetic and are probably not older than Late Cretaceous or early Tertiary.

These questions are treated in several related papers summarizing our lead isotope studies on the lead minerals and uranium ores of the Colorado Plateau. It is our present plan to submit these papers for publication in this journal.

L. R. STIEFF
T. W. STERN

WASHINGTON, D. C.,
March 3, 1959

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Economic Geology
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REVIEWS

Geology of the Manganese Deposits of Cuba, by FRANK S. SIMONDS and JOHN A. STRAZEK. Pp. 283; figs. 50. U. S. Geological Survey Bull. 1057, Washington, D. C. 1958. Price $6.00.

This report is a compilation and expansion of the results of investigations of Cuban manganese deposits by all geologists of the U. S. Geological Survey originally assigned to this war-time investigation. It concentrates heavily on the geology and deposits of southwestern Oriente, which are the most important. In this reviewer's knowledge there has never been so comprehensive a study of an entire manganese province, with so much observational data available; and the next publication promised by the authors in which they will take up the question of the origin of the manganese-bearing solutions and other theoretical questions, will be eagerly awaited.

This report combines a geological survey of a considerable part of southern Oriente Province with a detailed description of almost all of the manganese mines and prospects on the island. In all, there are descriptions of 172 mines, mine groups, or prospects, and these make up the bulk of the report. The principal purpose of the investigation was to assist the Cuban government in an examination of manganese resources, and these mine descriptions have been of major benefit to local mining organizations and individuals, who otherwise would have been working almost completely without knowledge of broad geological and distributive facts concerning the occurrence of manganese in the province as a whole. The report, therefore, is partly a mineral survey. However, its particular scientific value lies in the completeness of the field descriptions of the occurrence of manganese in a unique, large and well-exposed mineral province, representing a homogeneous geological system, which provides important clues to the genesis of manganese deposits in other similar regions.

The authors have established an incontrovertible point that the major deposits are syngenetic in origin. They occur in bedded sediments of dominantly volcanic origin and there is strong evidence that they are closely associated with thermal submarine springs.

Although manganese is associated with almost all of the mafic volcanic sequences on the island, the deposits in southern Oriente Province are of principal scientific and economic importance because they best demonstrate the relationship between mineralization and volcanic rocks and are the only significant producers.

Briefly, the principal physiographic features of this region are as follows. The southern edge of the province is dominated by the mountain ranges of the Sierra Maestra. North of this mountainous belt is a broad lowland area largely drained westward by the Rio Cauto known as the Cauto-Guantanamo lowland. This is a broad syncline, wedging eastward between the highlands of Sierra de Nipe and Sierra del Cristal to the north and the eastern ranges of the Sierra Maestra, and opening westward into the broad plain of the Cauto valley.

Of chief interest are the geological features of the thick section of bedded volcanics that make up most of the Sierra Maestra, and the continuation of these rocks

under the synclinal sediments of the lowlands area, with the northeastern limb overlapping the ultramafic cored highlands of Nipe-Cristal, well-known for their nickel, iron and chromium. The volcanics are inferred to extend throughout the central lowlands area, beneath a variable cover of non-volcanic sediments.

The volcanic formation of interest is the Cobre, of late Cretacious (?) to Middle Eocene age consisting of at least 4,000 m of andesitic, basaltic and dacitic tuff, agglomerate and lavas, and a prominent limestone bed, the Charco Redondo limestone member, at the top of the formation. All productive manganese deposits of Oriente are in the Cobre formation; mostly within a few tens of meters above or below the base of the Charco Redondo limestone member. They are found along this horizon at the top of the Cobre, exposed in the limbs of the syncline as it overlaps the southern flank of the Nipe-Cristal highlands and the northern flank of the Turquino and other ranges in the Sierra Maestra, and several domical structures in the lowlands area.

The authors believe that the bulk of the Cobre volcanic rocks are water-laid under submarine conditions, and that there were numerous volcanic vents distributed principally near the core of the Sierra Maestra. Of considerable interest is their belief that centers of volcanism also may have existed at the localities now marked by domical structures north of the mountains, such as in the Jutinicu, Sabanilla and Ponupo districts, and also near other groups of manganese deposits along the northeastern limb.

The primary ore deposits may be divided into bedded and non-bedded types, the former having yielded all but a small percentage of Cuba's manganese ore. The primary ores are psilomelane-type oxides, with supergene pyrolusite of importance locally. The bedded deposits are tabular bodies up to 1,000 ms long and 15 ms thick, commonly roughly elliptical in outline, and containing up to 45 percent Mn unless enriched by oxidation near the surface. They are generally much smaller and lower grade, mostly lying along pyroclastic beds with ore minerals occurring in an altered tuff or agglomerate matrix. In places the pyroclastic bed is within limestone (generally the Charco Redondo member). Closely associated with the deposits are extensive lenses of irregular masses of brown, red, or black jasper. The jasper generally underlies the ore, and almost invariably, the ore of highest grade is nearest the jasper.

Some of the most pertinent and detailed points relating to genesis and source of manganese listed by he authors in their summary discussions are as follows:

1. Bedded ores in tuffs and agglomerates generally show intense alteration of the gangue material to montmorillonitic clay in the immediate vicinity of the ore.
2. The association of manganese ores with jasper lenses is generally such that the ore appears to be following the development of the jasper.
3. The limited extent of individual ore bodies in roughly circular or elliptical lenses indicate local sources of the ore forming solutions, and not a pervasive deposition of the manganese such as in the case of iron formations.
4. These source locations appear to coincide with the large development of ferruginous silica. The highest grade ore is generally close to the jasper if it is present at all and grade diminishes away from the jasper lense.
5. The ore in most places is closely associated with volcanic tuff or agglomerate, even where the general host rock is limestone. The pyroclastic bed in this case is commonly co-extensive with the actual mineralization.
6. Intraformational conglomerates and breccias containing ore fragments from the underlying or adjacent bed together with clastic dikes cross cutting superimposed beds, and the development of stalactite-like replacement fea-

tures extending downward from ore beds into unconsolidated material below, but never upward, all indicate a syngenetic origin of the beds.

7. The universal development of psilomelane type minerals and the definite association of the oxidized form pyrolusite with surface agencies only, suggests that the ore was not deposited as a detrital material from some oxidized weathered source on a land surface.
8. The complete absence of manganese carbonate and minerals other than oxide suggests that the oxides are primary minerals.

From these and other evidences, the authors conclude that the deposits are of hypogene origin and that the ore-forming processes have not taken place uniformally over the entire manganese-bearing area but have been concentrated in a large number of relatively small areas. Furthermore, the deposits are syngenetic and were formed during or very shortly after the deposition of the beds along which they lie. Manganese solutions may have risen in volcanic vents as suggested by the fact that many bedded deposits including some in limestone are accompanied by very coarse tuff-agglomerate that could not have been deposited a great distance from its source. They believe that the most likely development of the manganese was by hot spring activity toward the end of the volcanism, and they point to the association of syngenetic deposits with structural domes having cores of coarse agglomerate. The source of the silica and iron in the jasper is concluded to be the same as that of the manganese, as is also the development of the alterations of the host rocks in the vicinity of ore.

It is interesting to note that the authors believe that the manganese was not derived from the volcanic rocks themselves, a question which the reviewer would like to suggest as the principal point of contention still left in the list of points that the authors have fairly conclusively settled. In their words, "The prominently bedded nature of much of the ore, the localized intense alteration of country rock, the great amounts of manganese concentrated in relatively small areas, and the occurrence of beds and irregular masses of essentially solid manganese oxide do not support the theory that the manganese was derived from the volcanic rocks themselves." The reviewer, over the past three years, has had an opportunity to examine many of the principal mines described by the authors, in particular, and in detail, the major deposit (the Charco Redondo) that is still operating. He wishes to state his almost complete concurrence with the field observations and almost all of the conclusions reached by the authors, and would like to raise minor points of differences only insofar as the discussion might promote investigation in the future.

The stratigraphy of the region has been greatly extended by the work of petroleum company geologists and some modifications are apparently needed as would be naturally expected. These details will have to wait for eventual publication by the geologists concerned.

The conclusion tentatively reached by the authors that the mineralizing hot spring solutions giving rise to the bedded ores derived their manganese from magmatic sources is questionable to the reviewer who would like to discuss it briefly only to keep the question open. There are over 100 known manganese occurrences within a broad stratigraphic horizon exposed by erosion around the central basin of the Province, representing both the north and south limbs of the major syncline, and around small domical structures within the basin. The fortuitous exposure of these manganese deposits suggests that there would be an abundance of unexposed deposits elsewhere in the synclinal area, and, in fact, there has been some evidence of this in deep drilling for petroleum. If it is not

assumed that the apparent association of deposits with the several domes (Jutinicu, Ponupo, El Aura, and others) which show some evidence of being volcanic vents, is necessarily evidence that the manganese was magmatic in origin, the authors' conclusion would be less pressing. Actually, it seems likely that, owing to original dips, coarseness of fragmentals and even possibly temperature distribution and trapped acid gaseous components, the volcanic vents might equally be the most logical centers of rising thermal waters that carried manganese leached from the volcanic rocks.

It seems difficult to assume nearby volcanic vents dotted along the line of outcrops of the particular horizon of interest in such regions as the anticlinal structures and faulted exposures extending many kilometers from the Santa Maria deposit to the Boston, and even continuing to the newly prospected Fetis claim to the southeast, or the dozens of kilometers of favorable horizon showing traces of mineralization up to workable deposits in the Guisa-Los Negros district, which have been exposed in most irregular fashion by erosion of the resistant Charco Redondo limestone. In short, the statistics of the occurrence of manganese rather strongly suggest that the development of hot springs was in itself a rather pervasive phenomenon, and, although causing localized deposits, generated such deposits in a rather random and very widely distributed form. Thus, rather than pointing to the localization of deposits around hot spring orifices as evidences for non-ubiquity of the deposits, the reviewer would prefer to observe the distributive aspect of the deposits themselves and say that the process of hot spring generation appears quite ubiquitous and essentially co-extensive with the basin of deposition of volcanic pyroclastics, particularly in the limbs where faulting due to compaction and settling is most likely to occur.

The literature abounds with discussion on the questions of the dissolution and separation of iron and manganese from various geological source materials, including thick sections of volcanic rocks (for summary of literature see Krauskopf, 1957). The most promising of these leaching and separation hypotheses should be rigorously tested by field evidences for the case of the Cuban deposits because it is in this region above all others that geological conditions are simple, homogeneous and abundantly repetitive for statistical testing. The region had no neighboring continental land mass and the only rocks possible as source materials were volcanics. The volcanics are thick, permeable, and rich in quickly chilled pyroclastic material that would be subject to easy dissolution and devitrification, probably yielding trapped acid components that would decrease the pH of the connate waters.

The fact that the deposits are restricted to the top of the volcanic section suggests repeated solution and deposition during the volcanic epoch, and this would favor processes for the gradual separation of the manganese from the iron, as solutions changed alternately from slightly acid and reducing to slightly alkaline and oxidizing by burial or mixing with circulating sea water. Although there is considerable iron in the jasper and alterations, it would be of major importance to find substantial amounts of secondary iron minerals in the body of the volcanic section itself (possibly in the form of silicates that are easily overlooked) that would permit relative manganese rich solutions to have formed the ores. The conclusion reached by Krauskopf, Garrels, Park and others that there is no reason to call on unknown magmatic sources for the origin of iron-free manganese ores, when understood processes capable of separating these components are available, is shared by the reviewer.

The authors state that the report represents only a resumé of the field evidence and that a more extensive consideration of all of the above questions will be forthcoming in a later report after completion of laboratory studies. This will complete an excellent and notable addition to our understanding of manganese deposits.

P. M. HURLEY

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
CAMBRIDGE, MASS.,
March 30, 1959

REFERENCE

Krauskopf, K., 1957, Separation of manganese from iron in sedimentary processes: Geochim. et Cosmochim. Acta: vol. 12, p. 61–84.

Cours de Cristallographie, Vol. I, Cristallographie géométrique. By R. GAY, Professeur à la Faculté des Sciences de Bordeaux. Pp. 253, figs. 108. Gauthier-Villars, Paris, 1958/1959. Price, f. 2900, $6.17.

This volume is the first of four. The second one, already in press, will be Physico-chemical Crystallography; the third, X-ray Crystallography; and the fourth, Crystal Physics. In this volume are two main parts, Geometrical crystallography, and Crystal structures; several appendices contain student exercises and important miscellaneous data. An alphabetical index (9 columns on 5 pages) and a three-page table of contents may be found at the end of the book. It is surprising to find so little reference to, or exercise of, the now generally used symmetry symbols of Hermann and Mauguin, as modified and adopted in the International Tables for X-ray Crystallography (Henry and Lonsdale, editors, Birmingham, 1952). (That the internationally recognized nomenclature for crystal forms and symmetry is widely used in all languages except French, is mentioned on p. 51.) Thus, although the course outlined in this textbook appears quite adequate, it may leave the French student with a small handicap for the study of the non-French literature of crystallography.

The approach to geometrical crystallography is essentially historical, and largely drawn from excellent, classical and standard French works. The too-abbreviated form symbols of Haüy and Levy are used throughout, with Miller symbols placed near many, but not all, of these.

Structural crystallography builds upon the geometrical section by "populating" —so to speak—various equipoint sets of selected space groups, and by outlining structures of various types, using mainly mineralogical examples.

The book is printed by offset from clearly typed copy with properly justified margins; it has few typographical errors. The illustrations are mostly well conceived and clearly reproduced. Those showing crystal structures might give an unwary student false impressions of the relative sizes of the elements but are clear and well chosen. The Wulff net reproduced on p. 225 measures 101.0 mm by 99.2 mm, and might better have been made diagrammatic, with circles 15°, instead of 2° intervals. Separate good nets are available cheaply on more stable paper, and would be more useful than the one reproduced.

As a whole, this book represents a satisfactory course in crystallography, which would need changes in emphasis and detail, but certainly not major changes, if it were to be used outside of France.

H. WINCHELL

GeoScience Abstracts. Vol. I, No. 1, Jan., 1959. Pp. 59. Amer. Geol. Inst., Washington, D. C., 1959.

This initial number of a new journal will be welcomed by the geological profession. It replaces Geological Abstracts, which was initiated in 1953 by the Geological Society of America acting for the A.G.I. through a grant from the National Science Foundation. The former publication consisted of photo-offsetting authors' abstracts sent in by the journals. The new journal is made up mainly of author abstracts sent in by the publishing organizations, but they are retyped for a two-column page and offset. The aim will be a complete coverage of geological literature published in North America. In addition, some Russian abstracts will be included.

The contents are divided into 15 sections, made up of the various geologic sciences and geophysics and geochemistry. This first number contains 291 abstracts. As the journal will appear monthly it is expected that 3,500 to 4,000 abstracts will appear the first year.

The subscription rates seem rather high. They are $15.00 to A.G.I. members for personal use only; $35.00 to non-A.G.I. members and libraries; and $65.00 for private organizations and government agencies.

The new journal has made a good start—good luck to it in the future.

The Atom and the Energy Revolution. By NORMAN LANSDELL. Pp. 200; pl. 32. Philosophical Library, New York, 1958. Price, $6.00.

The amount of news devoted to atomic power these days has created an interest among general readers to know more about it. This book attempts to serve that purpose and to give the layman a grasp of the social and political implications of this new source of energy. There is much in it for the specialist also.

In chapter I the world energy resources and demand is considered in general and in different countries. Chapter II describes the various sources of energy. The following 2 chapters deal with atomic energy—fission, fusion, controls, chain reactions, and reactors. The next 2 chapters consider the sources of atomic materials and the applications and world development of atomic power in various countries of the world. The remaining 3 chapters take up the political, commercial, national and international aspects, and the problems of radiation risk.

One does not need to be a scientist to read this interesting book.

Conservation of Natural Resources, 2nd Edit. Edited by GUY-HAROLD SMITH. Pp. 474. John Wiley & Sons, 1958. Price, $8.50.

Nineteen authors, each a specialist, have contributed to this large second edition. Five sections have been completely rewritten, a new chapter on "Economics and Conservation" has been added, and much new material and many illustrations have been incorporated in other chapters. There is considerable new material on agriculture, land reclamation and irrigation, mineral and manpower resources, and state and local planning.

As before, it is divided into eight parts—1, general; 2, soils, grasslands, irrigation, and reclamation; 3, forests; 4, water supply, water power, waterways, flood control; 5, mineral resources; 6, wildlife and fisheries; 7, recreational resources; and 8, state, local and national planning.

The volume has the same format and page size as its predecessor but has 78 fewer pages, due largely to the use of smaller type. It will continue to be an excellent reference book.

Geology of the Great Lakes. By JACK L. HOUGH. Pp. 313; figs. 75. Univ. of Illinois Press, Urbana, 1958. Price, $8.50.

The author first considers in Part I the geology of the Great Lakes region, the present lakes, and the pre-lake history. The first chapter is descriptive of the lakes, their depths, bottom topography and geologic setting. The next chapter considers the lake water—waves, tides, currents, fluctuations, circulation, precipitation and evaporation, and chemistry of the water. A third chapter is devoted to the lake sediments; a fourth is the preglacial history; and a fifth deals with the glacial history. A final chapter goes into the dating of the events of lake history.

Part II deals with the fascinating history of lake stages, from the earliest known lakes to the present. The early lake stages of each of the lake basins is first presented, followed by discussions of Lake Algonquin, post-Algonquin and Nipissing great lakes. The author then has a chapter on the transition from these lake stages to the present great lakes, illustrated by 22 lake stage maps. The final chapter brings together the radiocarbon chronology of the Great Lakes history.

The book is written largely for the lay reader, but students of geology will find assembled here within a single book much information that is now widely scattered in the literature. It is delightfully written and well illustrated with photos, drawings, and charts.

Explorations East of the High Andes (from Patagonia to the Amazon). By VICTOR OPPENHEIM. Pp. 267. Pageant Press, New York, Dec., 1958. Price, $5.00.

This is a book in which adventure and science go hand in hand, and some of the adventures are breathtaking. The author has travelled widely in all of these countries and has explored little known regions of Peru, Bolivia and the Argentine. He discusses the general geology, and the mineral resources of these regions, and refers also to oil reserve possibilities. In addition, one also gains insight into the ethnology, anthropology, etymology and history of these regions and peoples. Particularly interesting, however, are the descriptions of little known sections of the area, the early history of some of the countries, and of the peoples who inhabit the lands—the aborigines and the remnants of the Incas who peopled this vast empire.

The book gives the reader a better understanding of the peoples and of the countries of this great section of South America, and it is also a thrilling adventure story of a geologist in his explorations.

BOOKS RECEIVED

JOHN W. SALISBURY AND JOHN E. COTTEN

Automation and Society, ed. by H. B. JACOBSON and J. S. ROUCEK. Pp. 553. Philosophical Library, New York, 1959. Price, $10.00. *Thirty-two experts contribute articles on technological operations of automation and the intellectual and social effects.*

Suggestions to Authors of the Reports of the United States Geological Survey, 5th Ed. Pp. 225. Washington, D. C., 1959. *A larger revision with broader coverage. A necessary reference for all students, writers, reviewers, and editors.*

High Altitude and Satellite Rockets. A symposium sponsored by the Royal Aeronautical Society, The British Interplanetary Society and the College of Aeronautics held at Cranfield, England, July, 1957. Pp. 136; figs. 89; tbls. 17. Published by the Philosophical Library, New York, 1959. *Thirteen articles with discussions on all aspects of rocketry.*

Second Annual Report of the International Tin Council 1957–58. Pp. 24. Price, $1.00. International Tin Council, London, 1958. *Summary of the work of the Council in setting prices and quotas for tin.*

Miocene Diatom Assemblages from the Onnagawa Formation and Their Distribution in the Correlative Formations in Northeast Japan. TARO KANAYA. Pp. 130; pls. 15; figs. 6. Tohoku University, Sendai, Japan, 1959. *Sixty-four diatom forms were distinguished. They are distributed in 23 genera, and 50 species and varieties were identified, including eight new species. In English.*

Extract from Colombo Plan Report on Airborne Magnetometer and Scintillation Counter Survey over Parts of Perak, Selangor, and Negri Sembilan (Area 1). W. B. AGOCS and J. R. PATON. **Interpretative Summary** by J. B. ALEXANDER. Pp. 50; pls. 2; fig. 1. Price, $5.00 Malayan. Malayan Geological Survey Economic Bulletin C-1.1, Ipoh, 1958. *The survey indicates possible economic mineral deposits occurring at depth in certain limited parts of the area, but is not a full prospection report as no special note has been taken of possible superficial deposits. Different sections of the report are printed in different colors to produce a most attractive and useful effect, but the pagination is mystifying.*

Geological Maps. Students' Edition. Pp. 42; figs. 21. University of Tasmania Visual Aids Center Publ. 12S, Hobart, 1958. *A graded series of elementary exercises in the interpretation of geologic maps.*

Minerales. Pp. 124; pls. 11; figs. 21; tbls. 5. Revista Trimestral del Instituto de Ingenieros de Minas de Chile, Año XIII, No. 63, Santiago, 1958. *Nine articles on various aspects of mining and geology in Chile, plus a report on the last annual meeting of the Institute. In Spanish.*

The Bedrock Geology of the Guilford 15-Minute Quadrangle and a Portion of the New Haven Quadrangle. H. M. MIKAMI and R. E. DIGMAN. Pp. 99; pls. 23; figs. 12; tbls. 7. Connecticut Geological and Natural History Survey, Bull. 86, Hartford, 1957. *The crystalline rocks of the area display three foliation domes with igneous rocks in their cores and metasedimentary and metavolcanic rocks around them.*

Geology of North Tailevu, Viti Levu. R. E. HOUTZ. Pp. 19; pl. 1; figs. 10. Price, 10s. Fiji Geological Survey Bull. 1, Suva, 1958. *Zinc-copper-lead mineralization, carrying minor gold and silver, is vein-like in volcanics and replaces lime-rich beds.*

Étude Sédimentologique et Métallogénique de la Région Minière. GEORGES BIGOTTE. Pp. 188; pls. 24; figs. 45; tbls. 28. French Equatorial Africa Department of Mines and Geology, Bull. 9, Paris, 1959. *An exhaustive study of the copper, lead, zinc deposits of Boko-Songo.*

Transactions of the Mining, Geological and Metallurgical Institute of India, Vol. 54, No. 1. Pp. 110; pls. 2; figs. 36; tbls. 10. Price, Rs. 6. Calcutta, 1958. *Two papers on the inflammability of Indian coals, and the iron ore mines of Lappland, plus records and speeches of the fifty-first annual general meeting.*

Matemáticas Astronomía y Astrofísica Física Geología, Geofísica, Geodesia. Pp. 113. Boletin del Centro de Documentacion Cientifica y Tecnica de Mexico, Vol. VIII, No. 3, Seccion 1A, Mexico, 1959. *International bibliography of publications in these fields in 1958.*

The Ground-Water Resources of Chemung County, New York. W. S. WETTERHALL. Pp. 58; pl. 1; figs. 6; tbls. 4. New York Water Power and Control Commission Bull. GW-40, Albany, 1959. *Ground water in the county is of generally acceptable quantity and quality for domestic uses, though much of it is hard and higher in iron content than is desirable.*

Bibliography of the Geology and Natural Resources of North Dakota, 1814–1944, with Supplements—One and Two. C. E. BUDGE. Pp. 365; fig. 1. North Dakota Research Foundation Bull. 1, 1946. Reprinted by North Dakota Geological Survey, Grand Forks, 1959.

Anthracologic Analysis. A Guide to the Applied Petrology of Ohio Coals. G. H. CADY. Pp. 83; figs. 18; tbls. 6. Ohio Department of Natural Resources Information Circ. 22, Columbus, 1958. *The general purpose of this study has been to describe and evaluate various procedures and techniques available for use in the petrographic description and analysis of coal beds.*

List of Maps Outlined on Ontario Department of Mines Index Map No. 1958A. Pp. 13. Ontario Department of Mines Bull. 156, Toronto, 1959. *A list of maps—not publications. List of all publications in Bull. 25.*

Estudos, Notas e Trabalhos do Serviço de Fomento Mineiro. Pp. 64; pls. 14; fig. 1; tbls. 6. Geological Survey of Portugal, Vol. XIII, Nos. 1–2. *Three articles on iron, manganese and zinc deposits in Portugal. In Portuguese with one French and two English summaries.*

Records of the Geological Survey of Tanganyika, Vol. VI, 1956. Pp. 102; pls. 14; fig. 1; tbls. 35. Price, Shs. 17/50. Dar Es Salaam, 1958. *Twenty-one articles and three appendices covering progress reports and regional notes, economic geology, geophysics, petrology, and mineralogy.*

Annual Report of the Geological Survey Department for the Year Ended 31st December, 1958. Pp 18. Price, Shs. 2. Uganda Protectorate, Entebbe, 1959.

Caverns of West Virginia. W. E. DAVIES. Pp. 330; pl. 1; figs. 139. West Virginia Geological Survey Vol. XIX (A.), Morgantown, 1958. *Excellent descriptions and maps of caves with advanced discussion of cave origin.*

Divisão de Geologia e Mineralogia—Rio de Janeiro, Brasil, 1957–58.

Notas Preliminares e Estudos Nos. 98–107. *Preliminary short notes on fossils and stratigraphy.*

Avulso 81. Revisão da Estratigrafia Pré-Cambriana do Quadrilátero Ferrifero. J. DORR, J. E. GAIR, J. B. POMERENE, and G. A. RYNEARSON. Pp. 31. *Report sets up the main divisions of the Precambrian rocks, but leaves the naming and description of the individual formations to be created to 16 forthcoming papers. In Portuguese; English summary.*

Avulso 82. Reservas Estimadas de Minérios de Ferro no Quadrilátero Ferrífero, Minas Gerais. J. DORR. Pp. 28; pls. 3. *Total indicated high grade hematite 1,458,500,000 tons. Total concentratable itabirite, projected to 10M depth 4,698,700,000 tons. In both English and Portuguese.*

Bol. 97. Relatório da Diretoria 1959. A. I. ERICHSEN and I. C. DO AMARAL. Pp. 172; tbls. 5. *Summary of mineral production and geology of the deposits, district by district. In Portuguese.*

Bol. 103. Relatório Sôbre a Jazida de Pirocloro de Barreiro, Araxá, Minas Gerais. DJALMA GUIMARÃES. Pp. 87; pls. 25; tbls. 33. *In Portuguese.*

Bol. 105. Jazidas de Manganês de Minas Gerais, Brasil. J. DORR, A. HOREN, and I. S. COELHO. Pp. 95; pls. 6; tbls. 4. *Approximately 91.7% of Brazilian manganese production comes from Minas Gerais. In Portuguese.*

California Division of Mines—San Francisco, 1950–59.

Fifty-fifth Report of the State Mineralogist. G. B. OAKESHOTT. Pp. 244; figs. 30; tbls. 9. *The value of mineral production in California reached the all-time high of $1.65 billion in 1957. Petroleum products accounted for 77% of the value; nonmetallic minerals, 20%; and metals, 2.7%.*

Geologic Map of California, Alturas Sheet. T. E. GAY and Q. A. AUNE. *Map, scale 1:250,000, plus index map to geologic mapping used in compilation of the Alturas Sheet. Price, $1.50.*

Illinois Geological Survey—Urbana, 1959.

Circ. 267. Spar Mountain Sandstone in Cooks Mills Area, Coles and Douglas Counties, Illinois. L. L. WHITING. Pp. 24; figs. 7; tbl. 1. *The oil producing sand in the Illinois Basin commonly referred to as "Rosiclare" is older than true Rosiclare and is correlative with Spar Mountain Sandstone. The environment in which the Spar Mountain sediments were deposited resembled that on the Bahama Banks today.*

Circ. 268. Effect of Coal Inventories on Stability of the Coal Industry. H. E. RISSER. Pp. 11; figs. 6; tbls. 5. *Seasonal inventories tend to stabilize production while protective inventories accentuate fluctuations in coal production.*

Rept. of Investigations 210. Crevice Lead-Zinc Deposits of Northwestern Illinois. J. C. BRADBURY. Pp. 49; pls. 6, figs. 11; tbl. 1. *These shallow lead-zinc deposits are not now generally regarded as economically valuable, but evidence suggests that mineralization can be expected to occur at depths below those formerly mined. Geochemical prospecting methods appear most promising for renewed exploration.*

Geological Survey of Japan—Hisamoto-chō, Kawasaki-shi, 1958.

Explanatory Text of the Geological Map of Japan. Tsukigata (Sapporo-4). T. KAKIMI and T. UEMURA. Pp. 67; figs. 12; tbls. 10. Map, scale 1:50,000. *The area mapped covers the southern central part of the Kabato mountain land and is one of the type areas of Cenozoic sedimentary rocks occurring in the mountainland. In Japanese; English summary.*

Explanatory Text of the Geological Map of Japan. Hyuga-Aoshima (Kagoshima-84). Y. KINO. Pp. 68; figs. 31; tbls. 6. Geological map, scale 1:50,000. *The area mapped is referred to as the "Minami-nake mountainland," and the rocks are sedimentary and of Cenozoic age. In Japanese; English summary.*

Explanatory Text of the Geological Map of Japan. Higashimozumi (Kanazawa-36). M. KAWAI and T. NOZAWA. Map, scale 1:50,000. *Important deposits of gold, lead, and zinc occur in metamorphic rocks in the area which is located in the northeastern portion of the Hida plateau. In Japanese; English summary.*

Geological Survey of Kansas—Lawrence, 1959.

Bull. 134, Pt. 1. Description of a Dakota (Cretaceous) Core from Cheyenne County, Kansas. D. F. MERRIAM, W. R. ATKINSON, P. C. FRANKS, N. PLUMMER,

and F. W. PRESTON. Pp. 104; pls. 4; figs. 13; tbls. 11. *The 487-foot cored section extends from the lower part of the Graneros shale almost completely through the Dakota group into the Cheyenne sandstone. Lithologic descriptions are presented, as well as data on fossils, porosity and permeability, clay mineralogy, and other pertinent information.*

Bull. 136. Geology and Ground-water Resources of Clay County, Kansas. K. L. WALTERS and C. K. BAYNE. Pp. 106; pls. 7; figs. 14; tbls. 10. *Sedimentary rocks ranging in age from Permian to Recent crop out in Clay County. Unconsolidated sand and gravel deposits of Pleistocene age form the principal aquifer.*

Second Meeting, East-Central and Southern Regional Committee for Geology, Tananarive, Tanganyika, 1957.

A Brief Comparison between the Mica-bearing Pegmatites of the Uluguru Mountains and the Mikese Area, Morogoro District, Tanganyika. D. N. SAMPSON. Pp. 139–156. (Reprint.) *The writer believes the Uluguru pegmatites to be of magmatic origin, with more complex internal structures due to subsequent hydrothermal activity. The Mikese pegmatites, on the other hand, may possibly have originated from the host rocks.*

An Occurrence of Soapstone in a Migmatitic Environment, Central Province, Tanganyika. P. E. BROWN. Pp. 177–182. (Reprint.) *Zoned ultrabasic bodies occur in migmatitic granite gneiss. Two features of primary interest are the unusually great width of the actinolite zone and the absence of a biotite rim in the zoned bodies.*

Soapstone Bodies Produced by Magnesium Metasomatism in South-West Tanganyika. J. R. HARPUM. Pp. 183–192. (Reprint.) *Sheared amphibolites appear to have been altered in Ukinga times by metasomatic activity localized along an underlying major thrust.*

Geological Survey of Washington—Olympia, 1959.

Bull. 45. Washington's Channeled Scabland. J. HARLEN BRETZ. Pp. 57; pls. 4; figs. 36. Price, 50 cents. *Summary of Bretz' earlier ideas as well as his findings from more recent work in the areas.*

Information Circ. 31. Prospecting in Washington. D. L. ANDERSON. Pp. 26; figs. 9; tbls. 7. Price, free. *Report describes types of ore deposits and the minerals and rocks associated with them. Includes sampling methods, claim staking, and other sources of information.*

U. S. Geological Survey—Washington, D. C., 1958–59.

Bull. 1060-C. Geology and Construction-Material Resources of Pottawatomie County, Kansas. G. R. SCOTT, F. W. FOSTER, and C. F. CRUMPTON. Pp. 97–178; pl. 1; figs. 4; tbl. 1. *Pennsylvanian and Permian rocks crop out in the Nemaha range, a long narrow anticline. Construction materials available are concrete aggregate, road metal, mineral filler, riprap, and structural limestone.*

Bull. 1072-D. Quartz Crystal Deposits of Southwestern Virginia and Western North Carolina. J. B. MERTIE, JR. Pp. 233–298; figs. 6. Price, 55 cents. *Most of the quartz deposits occur in predominantly schist and gneiss terrain on the plateau that forms the northwestern flank of the Blue Ridge. Three modes of formation of quartz crystals are recognized.*

Bull. 1082-B. Radioactive Rare-Earth Deposit at Scrub Oaks Mine, Morris County New Jersey. K. KLEMIS, A. V. HEYL, JR., A. R. TAYLOR, and J. STONE. Pp. 29–59; pl. 1; figs. 6; tbls. 4. Price, 50 cents. *Discrete bodies of rare-earth-bearing magnetite ore apparently follow the plunge of the main magnetite ore body. Rare-earth minerals also occur in pegmatite adjacent to the magnetite.*

Bull. 1084-B. Rapid Analysis of Chromite and Chrome Ore. J. I. DINNIN. Pp. 31–68; figs. 4; tbls. 3. Price, 20 cents. *A discussion of rapid methods of laboratory analysis for determining the major and some minor constituents of chromite and chrome ore.*

Bull. 1086-D. Geophysical Abstracts 175 October-December 1958. DOROTHY B. VITALIANO, S. T. VESSELOWSKY, and others. Pp. 327–465. Price, 35 cents. *Abstracts of current literature pertaining to the physics of the solid earth and to geophysical exploration.*

Bull. 1019-M. Annotated Bibliography on the Geology of Selenium. GWENDOLYN W. LUTTRELL. Pp. 867–972; Pl. 1; fig. 1. Price, 50 cents. *References on geologic occurrence, mineralogy, geochemistry, metallurgy, analytical procedures, biologic effects, production and uses of selenium.*

Prof. Paper 272-B. The Effect of the Addition of Heat from a Powerplant on the Thermal Structure and Evaporation of Lake Colorado City, Texas. G. E. HARBECK, JR., G. E. KOBERG, and G. H. HUGHES. Pp. 7–51; pls. 2; figs. 22; tbls. 11. Price, 50 cents. *The lake, a reservoir in north-central Texas, is used as a source of cooling water for a thermal-electric powerplant. Increase in evaporation, when expressed as a volume, is directly proportional to the amount of heat added.*

Prof. Paper 294-K. The Rocks and Fossils of Glacier National Park: The Story of Their Origin and History. C. P. ROSS and R. REZAK. Pp. 401–439; pls. 3; figs. 23. *A simple, nontechnical explanation of the geological processes that created the magnificent scenery.*

Prof. Paper 299. Geology of the Arkansas Bauxite Region. M. GORDON, JR., J. I. TRACEY, JR., and M. W. ELLIS. Pp. 268; pls. 39; figs. 63; tbls. 15. *Description, classification, and origin of the bauxite deposits, and their geologic setting relative to an early Eocene land surface. Geologic map, scale 1:31,680.*

Prof. Paper 305-G. Test Wells, Titaluk and Knifeblade Areas, Alaska. FLORENCE M. ROBINSON. **Micropaleontologic Study of Test Wells in the Titaluk and Knifeblade Areas, Northern Alaska.** H. R. BERGQUIST. P. 377–422; pls. 4; figs. 5. Price, $1.00. *Four test wells were drilled on two anticlines to test sandstone of the Grandstand formation of Cretaceous age. Except for a few minor shows of gas and oil, the tests were dry.*

Prof. Paper 305-H. Test Wells, Square Lake and Wolf Creek Areas Alaska. FLORENCE R. COLLINS. **Micropaleontology studies** by H. R. BERGQUIST. Pp. 423–484; pls. 2; figs. 6. Price, $1.00. *Noncommercial amounts of gas and oil were discovered in some sand horizons penetrated by four test wells in Naval Petroleum Reserve No. 4.*

Prof. Paper 305-J. Test Wells Simpson Area Alaska. FLORENCE M. ROBINSON. **With a section on Core Analysis** by S. T. YUSTER. Pp. 523–568; pls. 4; figs. 5; tbls. 5. Price, $1.25. *Two test wells, one dry and the other with fair shows of oil (not of commercial value), were drilled in the Cape Simpson area, northern Alaska, in conjunction with the exploration of Naval Petroleum Reserve No. 4.*

Prof. Paper 314-E. Classification, Delineation and Measurement of Nonparallel Folds. J. B. MERTIE, JR. Pp. 91–124; figs. 12. Price, 30 cents. *Stratigraphic traces of most nonparallel folds, in sections selected to show the maximum or minimum curvature, may be represented approximately by one or more families of curves that are analytically related.*

Prof. Paper 314-F. Sedimentary Studies in the Middle River Drainage Basin of the Shenandoah Valley of Virginia. DOROTHY CARROLL. Pp. 125–154; pls. 2; figs. 8; tbls. 12. Price, 70 cents. *Significance of mineralogy and grain-size distribution of materials in a drainage basin.*

Water-Supply Paper 1475-A. Hydrologic Data Wind River and Fifteen Mile Creek Basins, Wyoming 1947–54. N. J. KING. Pp. 1–44; pls. 6; figs. 9; tbls. 13. *Owing to the lack of high intensity storms and associated runoff within the project areas during this period, the data are insufficient to warrant conclusive interpretations; the report is, therefore, in effect a progress report.*

Economic Geology
Vol. 54, 1959, pp. 766–768

SCIENTIFIC NOTES AND NEWS

Note to our contributors: Authors' reprints are run off at the same time as the issue of ECONOMIC GEOLOGY in which a paper appears, but because of the volume of orders received by our printer, it takes a month to six weeks to process and mail them out. Once an issue of ECONOMIC GEOLOGY is run off, together with all reprints ordered by the authors, the type is knocked down, and it is for this reason that we cannot fill orders for reprints received after a paper has been published.

The EIGHTH NATIONAL CLAY CONFERENCE will be held on the University of Oklahoma campus at Norman, Oklahoma, on October 12, 13, and 14, under the auspices of the Clay Minerals Committee of the National Academy of Sciences-National Research Council. A field trip will be arranged to the Wichita Mountains to visit clay occurrences of geological interest. Two symposia of invited papers will be held on the subjects of "Clay-Water Systems" and "Clay Mineral-Geochemical Prospecting Methods." Those having contributions should contact Prof. C. G. Dodd, Chairman, University of Oklahoma, Norman, Oklahoma.

R. T. BRANDT has joined Mufulira Copper Mines, Ltd., as geologist.

JOHN R. RAND, the first full-time state geologist of Maine and secretary of the Maine Mining Bureau, is resigning on June 30 to return to private practice.

RICHARD M. FOOSE is now chairman of the department of earth sciences, Stanford Research Institute, Menlo Park, Calif.

ROBERT A. METZ, a geologist for Kennecott Copper Corp.'s Chino Mines Division, Santa Rita, N. M., has been named senior geologist for Kennecott's Ray Mines Division, Ray, Ariz., replacing JACQUES B. WERTZ of Superior, who resigned to accept a fellowship at the University of Arizona where he will work for his doctorate degree.

EVAN JUST who now heads the International Drilling and Water Co., Inc., will become a professor and head of Stanford University's Department of Mineral Engineering and take over his new teaching duties next fall. Mr. Just was previously vice president of Cyprus Mines Engineering and Mining Journal, a post he held for nearly ten years. On leave from this publication in 1957–58, he served as director of the ECA's Strategic Materials Division.

WILLIS M. JOHNS, geologist for the Montana Bureau of Mines in Kalispell, is currently working with the Pacific Power and Light Co. and the Great Northern Railway in a program to investigate raw materials in western Montana.

H. C. GUNNING has been appointed consulting geologist (Rhodesia) in the Salisbury office of Anglo American Corporation of S. A. Ltd. He succeeds DR. T. D. GUERNSEY who has retired.

The Department of Geology at the University of Notre Dame had DR. STANLEY E. JEROME, District Geologist, Northwest District, Bear Creek Mining Company, Salt Lake City, Utah, visit the Department on a three-day lecture series as part of the American Geological Institute Visiting Geoscientist Program for 1959 which is subsidized by the National Science Foundation. Dr. Jerome lectured during April 15–17 on the following subjects: Relations of Hypogene Mineral Deposits to Regional Tectonics; Colored Slide Air Obliques of Mining Districts of the Southwest; Geology and Exploration of Porphyry Copper Deposits; Influence of Structure in Mineral Deposits; and Colloquium on Mining and Mineral Exploration.

JOHN J. COLLINS, formerly associated with American Smelting and Refining Co., has been named general manager of Revere Copper & Brass Inc.'s new mining department which will develop ore sources, including bauxite.

RONALD K. SOREM, post-doctoral fellow in economic geology research at the University of Wisconsin and former U.S.G.S. geologist, has been appointed assistant professor at the State College of Washington, Pullman, effective September 16, 1959.

THOMAS A. HENDRICKS resigned June 1 as Director of Geological Research, Pan American Petroleum Corporation, to accept a staff position with the Fuels Branch of the U. S. Geological Survey, Denver, Colo.

The Fiftieth Anniversary Volume of ECONOMIC GEOLOGY, soon after its publication, was translated into Russian, the first Russian edition (under the title *Problemy Rudnykh Mestorozhdenii*) appearing in 1957. It is now announced in *Novye Knigi* that a second Russian edition will be published in Moscow about mid-1959.

JOHN R. FANSHAWE with his partner HOWARD R. LOWE, announce the firm of Northern Consultants at Billings, Montana.

H. C. B. LEITCH has joined the firm of Hill, Starck and Associates, consulting geologists, 844 West Hastings St., Vancouver, B. C.

REGINALD G. RYAN has resigned as chairman of the department of geology at Midwestern University. He will be associated with Ryan, Hutchinson and James, a new firm of consulting geologists in Wichita Falls, Texas.

STEWART E. POET, formerly a geologist for the St. Joseph Lead Co., now is self-employed in mining at Cripple Creek, Colo.

JOHN B. KNAEBEL has been appointed president and managing director of Anaconda Iron Ore Ltd.

DAVID SHARPSTONE, mining consultant, is now in Toronto after spending ten months on professional work in Ethopia, the Rhodesias, and Uganda.

E. WILLARD BERRY, professor in the geology department at Duke University, Durham, N. C., is studying the coals of Australia this summer. He wiil return to the U. S. in September.

JOHN E. RIDDELL, formerly associate professor in the department of geological sciences at McGill, has become professor and chairman of the department of geology at Carleton University, Ottawa, Ontario.

JOHN W. SVANHOLM has completed a second contract term for the Burmese Government, the Mineral Resources Development Corp., as consultant.

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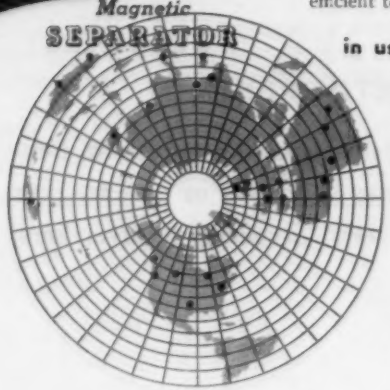

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